Structural Effects on Valence Tautomerism. Part 5.[1] A Carbon-13 Nuclear Magnetic Resonance. Study on the Effects of the π-Acceptor Ability of Aryl Substituents on the Valence Tautomerism of 7-Aryl-2,5-di-t-butylcyclohepta-1,3,5-trienes

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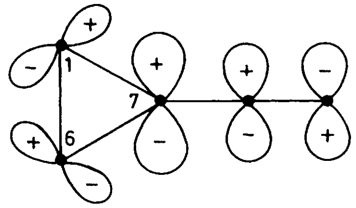
The cycloheptatriene (CHT)–norcaradiene (NCD) equilibria of eight 7-aryl-2,5-di-t-butylcyclohepta-1,3,5-trienes in CS_2–CD_2Cl_2 have been studied with the use of variable-temperature ^{13}C n.m.r. The equilibrium constants (K = [NCD]/[CHT]) below the coalescence temperatures were calculated from signal intensities; those at higher temperatures were obtained by use of the equation $K = (\delta_{CHT} - \delta)/(\delta - \delta_{NCD})$. The enthalpy ($\Delta H^0$) for the conversion of the CHT into the NCD tautomer decreases in the substituent order p-MeO > p-Me > H > p-Br ~ p-Cl > m-Cl > p-CF_3 > m,m'-Cl_2, with the ΔH^0 values for p-MeO and m,m'-Cl_2 2.64 ± 0.11 and −0.81 ± 0.13 kJ mol^{-1}, respectively. The ΔH^0 values are linearly correlated not only with the Hammett σ-constants, but also with the π-acceptor ability (the D value) of the aryl carbon atom adjacent to C(7) as estimated by INDO calculations; this supports Hoffmann and Günther's donor–acceptor theory. The ^{13}C signals of C(3) and C(4) in both the NCD and the CHT tautomer undergo downfield shifts as the D value of the aryl group increases; the shift of the former is 4.3 times more sensitive than that of the latter as evaluated by the Hammett plot. In addition, the difference in the ^{13}C shift of the *para*-carbon atom between the NCD and the CHT tautomer is larger in the 7-(m,m'-dichlorophenyl) than in the 7-phenyl system. These results suggest that conjugative interaction between the cyclopropane ring in the NCD structure and the aryl group increases with increase in the π-acceptor ability of the aryl group.

Interest in the structural dependence of the tautomerism between cyclohepta-1,3,5-triene (CHT) derivatives and their bicyclo[4.1.0]hepta-2,4-diene (norcaradiene; NCD) tautomers dates back to the proposal of the NCD structure for ' Buchner's ester '.[2] Very recently, the spectrophotometric detection of the elusive parent norcaradiene (C_7H_8) has been reported.[3] In the meantime, various factors have been found to affect the CHT–NCD equilibrium.[2] In particular the synthesis of 7,7-dicyanonorcaradiene by Ciganek[4] showed the marked effect of an electron-withdrawing substituent at the 7-position in shifting the equilibrium to the NCD side. However, despite the accumulated examples, the factors favouring the NCD tautomers have not been notably clarified.[2b,5] In particular it has been difficult to determine the individual electronic and steric effects of the substituent at C(7).[2b,6]

In 1970, the marked effects of unsaturated, electron-withdrawing 7-substituents such as CN, CO_2H, or CHO in stabilizing the NCD tautomer were explained by Hoffmann[7] and Günther[8] in terms of electron donation from the Walsh orbital of the cyclopropane ring in the NCD structure towards low lying unoccupied π MOs of the unsaturated substituent [equation (1)]. Because the Walsh orbital is antibonding between C(1) and C(6), this electron delocalization was interpreted as strengthening the C(1)–C(6) bond.[7,8] The order of effectiveness (CHO > CO_2H > CN)[9–11] and the existence of 7,7-bis(trifluoromethyl)cycloheptatriene in the CHT form,[12] where the 7-substituents are *saturated* electron-withdrawing groups, supported their theory; however, in this series also, the steric problem is not rigorously eliminated.



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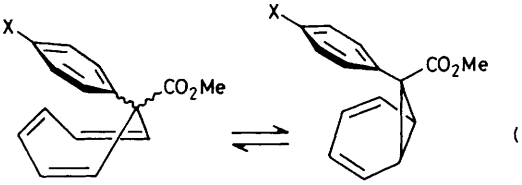

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One of the most familiar tests of electronic effects is to examine *meta* or *para*-substituents on aryl derivatives, in which the steric effect can be kept essentially constant. Hall and Roberts examined the equilibria of *para*-substituted 7-aryl-7-methoxycarbonylcycloheptatrienes [equation (2)], and found the ΔH° values for the conversion of the NCD into the CHT tautomer to be 9.6, 23, and 15 kJ mol^{-1} for p-MeO, H, and p-NO_2, respectively.[13] This irregular trend was once interpreted to render the MO interpretation untenable in a general way.[5]

Meanwhile, Günther and his co-workers showed that the system of Hall and Roberts was unsuitable for examining the conjugative interaction between the cyclopropane ring and the aryl group, because the latter is actually oriented *endo* and cannot assume a bisected conformation which is favourable for maximum conjugation.[14] Presumably, the more stabilizing methoxycarbonyl group is given priority in occupying the *exo*-orientation in the NCD tautomer. Of course, the most ideal system is the parent 7-arylcyclohepta-1,3,5-triene, but unfortunately 7-phenyl-[15] and other 7-aryl-cycloheptatrienes[16] exist essentially as the CHT tautomers (although recent work on their reaction with $^1O_2$ revealed qualitatively that the population of the NCD form increases in the order p-MeO < H < p-Cl[17]).

In our structural studies on cycloheptatriene derivatives, we found marked effects of t-butyl substituents at positions 2 and 5 in driving the equilibrium to the NCD side, presumably

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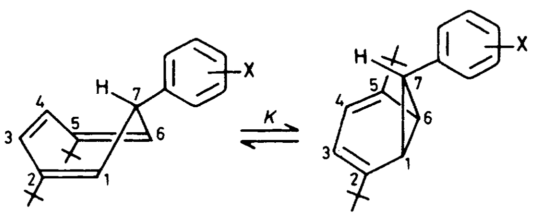
Table 1. Carbon-13 chemical shifts of the ring carbon atoms of 7-aryl-2,5-di-t-butylcyclohepta-1,3,5-trienes in CS_2–CD_2Cl_2 (3 : 1 v/v) at 25.00 MHz and at −117 and 23 °C

Substituent	Temp. (°C) [a]	Tautomer	Chemical shifts (Hz) [b] C(1,6)	C(2,5)	C(3,4)	C(7)
p-MeO	−117	CHT	3 117.7	3 574.2	3 280.0	1 109.6
		NCD	781.3	3 632.8	2 813.7	583.5
	23	CHT $\rightleftharpoons$ NCD	2 506.1	3 597.4	3 162.8	970.5
p-Me	−117	CHT	3 118.9	3 575.4	3 281.3	1 121.8
		NCD	794.7	3 635.3	2 818.6	594.5
	23	CHT $\rightleftharpoons$ NCD	2 391.4	3 602.3	3 140.9	957.0
H	−117	CHT	3 112.8	3 577.9	3 280.0	1 132.8
		NCD	802.0	3 634.0	2 819.8	601.8
	23	CHT $\rightleftharpoons$ NCD	2 343.8	3 604.7	3 133.5	957.0
p-Cl	−117	CHT	3 098.1	3 584.0	3 282.5	1 116.9
		NCD	805.7	3 630.4	2 824.7	594.5
	23	CHT $\rightleftharpoons$ NCD	2 363.3	3 585.2	3 142.1	949.7
p-Br	−117	CHT	3 096.9	3 585.2	3 282.5	1 119.4
		NCD	809.3	3 632.8	2 824.7	596.9
	23	CHT $\rightleftharpoons$ NCD	2 343.8	3 610.8	3 139.6	947.3
m-Cl	−117	CHT	3 088.4	3 587.7	3 282.5	1 125.5
		NCD	811.8	3 631.6	2 827.2	600.6
	23	CHT $\rightleftharpoons$ NCD	2 298.6	3 612.1	3 131.1	944.8
p-CF_3	−117	CHT	3 085.9	3 592.5	3 283.7	1 130.4
		NCD	826.4	3 635.3	2 832.0	610.4
	23	CHT $\rightleftharpoons$ NCD	2 172.9	3 618.2	3 109.1	921.6
m,m'-Cl_2	−117	CHT	3 066.4	3 596.2	3 284.9	1 119.4
		NCD	822.8	3 626.7	2 834.5	601.8
	23	CHT $\rightleftharpoons$ NCD	2 252.2	3 618.2	3 129.9	933.8

[a] Controlled to ±1 °C. [b] Chemical shifts from Me_4Si obtained by using δ 192.24 for CS_2 at resolution 1.2 Hz.



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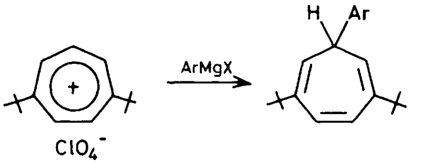

+ isomers (4)

owing to an increase in steric strain around the CHT ring and concomitant further bending of the ring.[1,18] Fortunately, the 7-aryl-2,5-di-t-butylcycloheptatrienes were found to exist in equilibrium with their NCD tautomers in such compositions as to permit ready observation of both CHT and NCD tautomers by low-temperature ^{13}C n.m.r.[1b] Moreover, it was found that the system contains only two tautomers, with the aryl group oriented equatorially in the CHT and *exo* in the NCD structure [equation (3)].[1b]

In a preliminary communication we reported on the primary dependence of the equilibrium position and the $\Delta H°$ value upon the π-acceptor ability of the *p*-methoxy-, *p*-trifluoromethyl-, or unsubstituted phenyl group on the 7-position as calculated by the INDO method.[1b] This paper provides a full account of the equilibrium study by variable-temperature ^{13}C n.m.r., INDO calculations, and correlations of the thermodynamic parameters with the π-acceptor ability of the aryl group containing the substituents *p*-MeO, *p*-Me, H, *p*-Cl, *m*-Cl, *p*-Br, *p*-CF_3, and *m,m'*-Cl_2.

Results

Syntheses.—All the compounds were prepared as solids by the reaction of 1,4-di-t-butyltropylium perchlorate [1b,19] with Grignard reagents [equation (4)], followed by recrystallization or h.p.l.c. ^1H N.m.r. data recorded at 35 °C and m.p.s are given in the Experimental section.

^{13}C *N.m.r. Spectra.*—The ^{13}C n.m.r. spectra were measured at 25.00 MHz for solutions in CS_2–CD_2Cl_2 (3 : 1 v/v) at temperatures over a range from −142 to +23 °C. Recently, Lambert *et al.* questioned the use of Me_4Si as a standard in variable-temperature ^{13}C n.m.r., when the temperature-dependent chemical shifts are used to calculate the equilibrium constant.[20] In the present study carbon disulphide (δ 192.24) was taken as the standard, since its signal showed an almost constant position down to −142 °C. In each compound, only time-averaged signals were observed at room temperature; as the temperature was lowered, each signal split into two, corresponding to the two tautomers of equation (3). No evidence for the existence of other conformational or configurational isomers was obtained. The chemical shift data for the individual tautomers at −117 °C and those for the equilibrating system at 23 °C are shown in Table 1. As a typical example the spectra of the 7-phenyl-2,5-di-t-butylcycloheptatriene tautomers are shown in Figure 1. Assignments were based on off-resonance spectra, signal intensities, and evaluation of the constancy of the splitting ratios $(\delta_{CHT} - \delta)/(\delta - \delta_{NCD})$.

^1H *N.m.r. Spectra.*—Figure 2 shows the ^1H n.m.r. spectra of 7-phenyl-2,5-di-t-butylcycloheptatriene tautomers at various temperatures as a typical example. As the temperature was

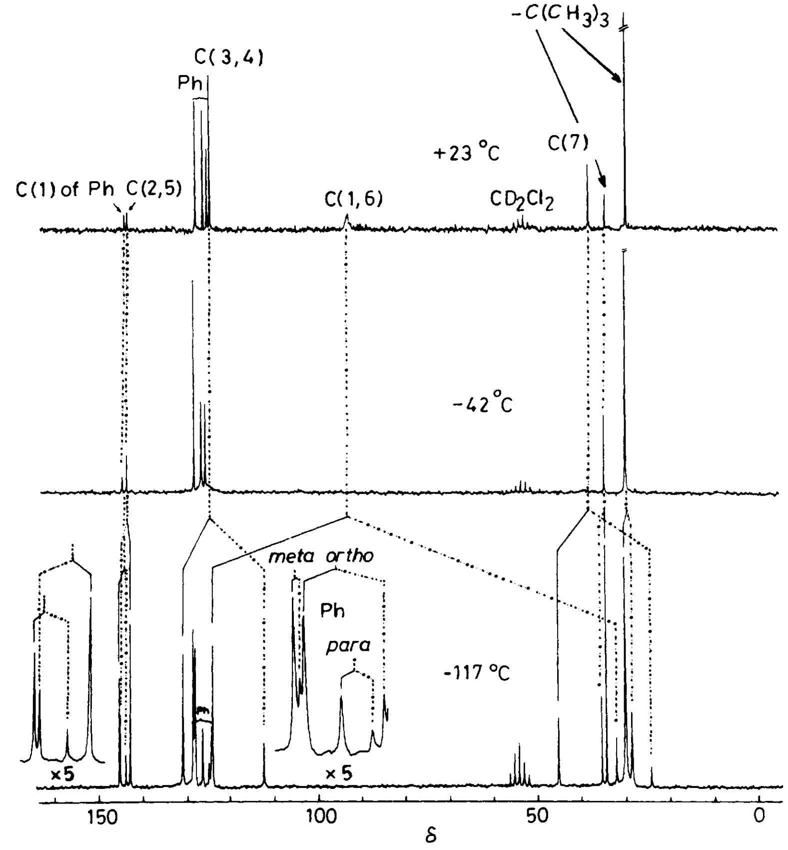

Figure 1. ^{13}C N.m.r. (25.00 MHz) spectra of 7-phenyl-2,5-di-t-butylcyclohepta-1,3,5-triene in CS_2–CD_2Cl_2 (3 : 1 v/v) at various temperatures: the solid and the dotted lines represent the signals assigned to the CHT and NCD forms, respectively

Table 2. Equilibrium constants (K) for the valence tautomerism of 7-aryl-2,5-di-t-butylcyclohepta-1,3,5-trienes in CS_2–CD_2Cl_2 (3 : 1 v/v) at various temperatures

	Substituents [b]							
Temp.[a] (°C)	*p*-MeO [c]	*p*-Me	H [d]	*p*-Cl [e]	*p*-Br	*m*-Cl	*p*-CF_3	*m*,*m*′-Cl_2
−142		0.178	0.212	0.227		0.468	0.764	
−130		0.186	0.266	0.277		0.502	0.733	0.795
−117	0.136	0.206	0.290	0.274	0.307	0.508	0.748	0.770
−106			0.297		0.323		0.739	0.739
−42		0.409		0.405	0.427			
−29	0.289	0.425	0.481	0.433	0.473	0.508		0.626
−17	0.309	0.431	0.493	0.437	0.479	0.527	0.718	0.608
0	0.326				0.486		0.686	
23	0.346					0.511	0.658	0.550

[a] Controlled to ±1 °C. [b] Standard deviations in the equilibrium constants are ±0.02—0.05 at below −100 °C and *ca.* ±0.01 above −60 °C. [c] $K = 0.124$ at −124 °C. [d] $K = 0.495$ at 9 °C. [e] $K = 0.403$ at −55 °C.

lowered, each signal broadened and then split into two after passing a coalescence point. In harmony with the observation by ^{13}C n.m.r., no signals indicating the existence of tautomers other than those in equation (3) were observed.

Equlibrium Constants and Thermodynamic Parameters.—The populations of the NCD and CHT forms were determined from the ^{13}C n.m.r. spectra in the following manner. The populations at lower temperatures were calculated from the heights of several signal pairs before broadening and then averaged. Generally four or five signal pairs were employed, affording a standard deviation of ±0.02—0.05 in the equilibrium constant.* At higher temperatures after coalescence had begun the equilibrium constants were calculated by applying the equation $K = (\delta_{CHT} - \delta)/(\delta - \delta_{NCD})$ to the signals of C(1), C(6), C(3), C(4), and C(7) with standard deviations of *ca.* ±0.01. The chemical shifts, δ_{CHT} and δ_{NCD}, were estimated by extrapolating the plots of those determined in the range from −142 to −91 °C against temperature. The equilibrium

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* A ^{1}H n.m.r. spectrum for the 7-phenyl system at −107 °C gave $K = 0.33 \pm 0.02$. This agrees well with the value (0.31 ± 0.02) obtained by interpolation in the ln$K$ *vs.* $1/T$ plot based on the ^{13}C n.m.r. method, supporting the validity of the present method.

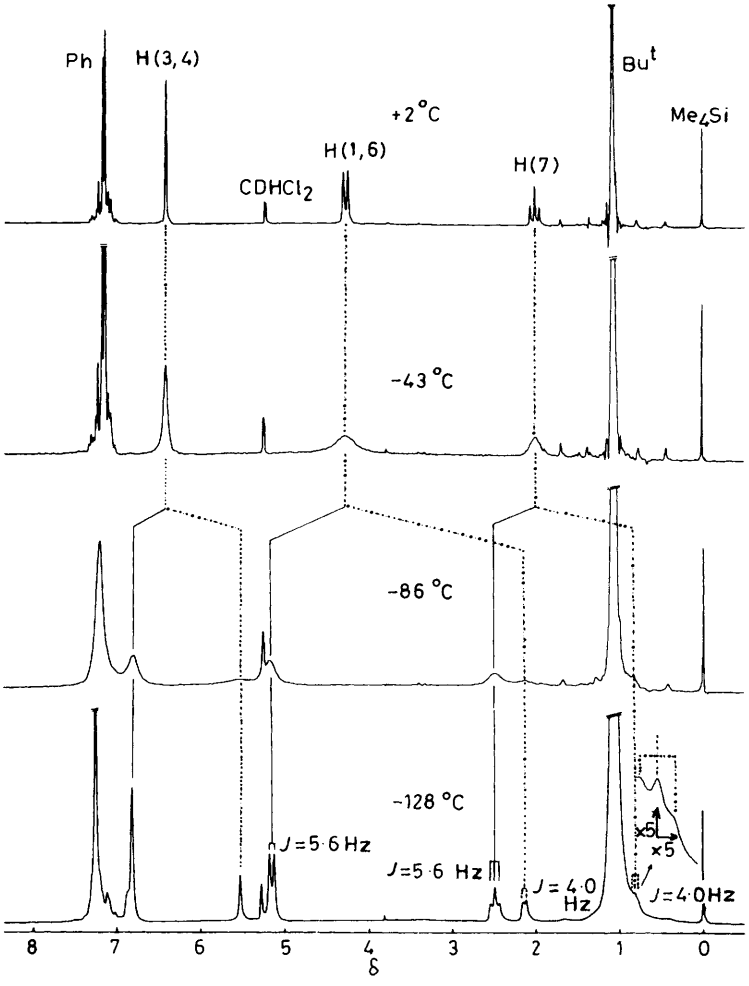

Figure 2. ^{1}H N.m.r. (99.55 MHz) spectra of 7-phenyl-2,5-di-t-butylcyclohepta-1,3,5-triene in CS_2–CD_2Cl_2 (3 : 1 v/v) at various temperatures: the solid and the dotted lines represent the signals assigned to the CHT and NCD forms, respectively

constants at various temperatures are shown in Table 2. From the plot of ln$K$ (K = [NCD]/[CHT]) values against $1/T$ the thermodynamic parameters, ΔH° and ΔS°, were calculated at the 90% confidence level and the results are summarized in Table 3. The values for p-MeO, H, and p-CF_3 are slightly different from those reported previously,[1b] owing to the improved accuracy of the measurement.

INDO Calculations.—The ability of the $p\pi$ atomic orbital in an aryl fragment to accept electrons can be estimated by the D value, which is defined by equation (5) [21] where C_{jr} is the

$$D = \sum_{j}^{\text{uno}} C_{jr}^2/(\varepsilon_j - \varepsilon_\sigma - \lambda) \qquad (5)$$

coefficient of the atomic orbital in the unoccupied πMO φ_j, ε_j and ε_σ denote the energies of the aryl πMO and the antisymmetric occupied Walsh orbital of the cyclopropane ring, respectively, and λ stands for the repulsion between a pair of electrons populated in these MOs. In this work the C_{jr} and ε_j values were calculated for various substituted benzenes (except for bromobenzene) by the INDO SCF MO method, and the ε_σ and λ values estimated to be -0.5 to -0.6 and 0.1—0.2 atomic units, respectively.* As to ε_σ, an INDO calculation for cyclopropane afforded a value of -0.527. The D values were calculated for the two cases, $-\varepsilon_\sigma - \lambda = 0.5$ and 0.3 with regard to the aryl carbon atom adjacent to C(7), and are tabulated (Table 3).

Discussion

Linear Correlation of π-Acceptor Ability (D) *with the Hammett σ-Constants.*—The plots of D values against Hammett σ-constants [23] yield fair linear correlations, with the correlation coefficient 0.9689 or 0.9644 for $-\varepsilon_\sigma - \lambda = 0.3$ or 0.5, respectively, suggesting that the σ-constants may also be usable as a measure of the π-acceptor ability of the aryl groups. Figure 3 shows a plot for the case $-\varepsilon_\sigma - \lambda = 0.3$. It has been reported that the pK_a values of various benzoic acids are linearly correlated with enthalpy (and also with entropy) of the dissociation equilibrium.[24] Therefore, the examination of the correlation of the D values, which are relevant to potential energy, with the σ-constants is reasonable.

Orientation of the Aryl Substituents.—Although the preferential equatorial orientation of the 7-phenyl group in 7-phenylcycloheptatriene is well known,[15] its orientation in the elusive NCD tautomer has not been established. In the present study comparison of the ^{1}H n.m.r. spectra of 7-phenylcyclo-

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* The calculations were performed on a FACOM M382 computer using the bond lengths and angles collected by Sutton.[22]

Table 3. The $\Delta H°$ and $\Delta S°$ values for the conversion of the CHT into the NCD tautomer, and π-acceptor abilities (D) of the aryl groups

Sub-stituent	$\Delta H°$ [a]/ kJ mol^{-1}	$\Delta S°$ [a]/ J K^{-1} mol^{-1}	π-Acceptor ability (D) [b] $-\varepsilon_\sigma - \lambda = 0.3$	π-Acceptor ability (D) [b] $-\varepsilon_\sigma - \lambda = 0.5$
p-MeO	2.64 ± 0.11	0.3 ± 0.1	0.9194	0.6623
p-Me	2.21 ± 0.34	1.7 ± 1.9	0.9547	0.6855
H	1.74 ± 0.16	0.6 ± 0.8	0.9655	0.6932
p-Cl	1.44 ± 0.18	−1.1 ± 0.9	0.9863	0.7020
p-Br	1.48 ± 0.17	−0.4 ± 0.8		
m-Cl	0.13 ± 0.14	−5.0 ± 0.7	1.0110	0.7183
p-CF_3	−0.22 ± 0.11	−3.9 ± 0.6	1.0622	0.7464
m,m'-Cl_2	−0.81 ± 0.13	−7.4 ± 0.6	1.0558	0.7426

[a] The standard errors are at the 90% confidence level. [b] See equation (5).

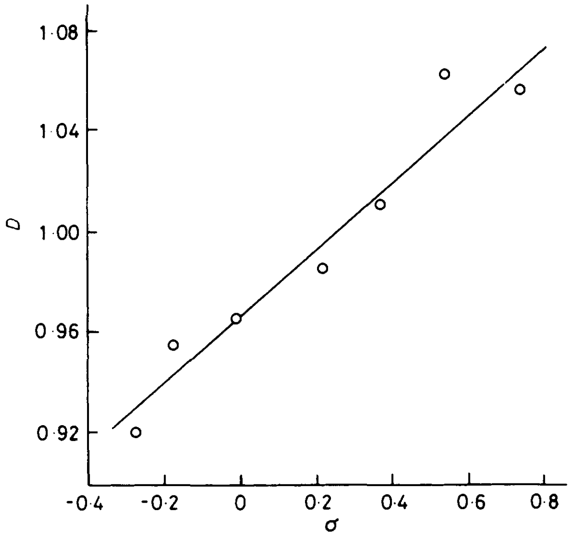

Figure 3. A plot of D values against the Hammett σ-constants: $-\varepsilon_\sigma - \lambda = 0.3$

heptatriene,[15a] 7-phenyl-2,5-di-t-butylcycloheptatriene and its NCD tautomer, and cyclopropylbenzene[25] permitted determination of the orientation. As shown in Figure 2, the H(7) signal of the CHT tautomer exhibits δ 2.49, similar to that of H(7) (δ 2.68)[15a] of 7-phenylcycloheptatriene. In the same spectrum, the H(7) signal of 7-phenyl-2,5-di-t-butylnorcaradiene appears at δ 0.80 (t, J 4.0 Hz). This upfield shift as compared with the δ value (1.71) of the H(1) signal of cyclopropylbenzene[25] indicates the *endo*-orientation of H(7), which is highly shielded by the C(2) and C(4) double bonds. The coupling constant (4.0 Hz), similar to J_{trans} (6.30 Hz) rather than J_{cis} (9.45 Hz) of cyclopropylbenzene,[25] also supports the *endo* orientation of H(7). Consequently, the equilibrium of the present system can be depicted by equation (3).

Equilibrium Constants.—In order to examine whether the equilibrium constants (K) can be used as a quantitative measure of the π-acceptor ability of the aryl groups, K values at −150 and 50 °C were estimated from the regression lines for the plots of ln K *vs*. $1/T$, and the order amongst the various substituents was investigated. At −150 °C the order is m,m'-Cl_2 (K 0.904) > p-CF_3 (0.770) > m-Cl (0.482) > p-Br (0.224) > p-Cl (0.214) > H (0.199) > p-Me (0.129) > p-MeO (0.079). This order is in harmony with that expected from the π-acceptor ability of the aryl group with the exception of m,m'-Cl_2 and p-CF_3. On the other hand, at 50 °C the order is quite irregular; the equilibrium constants are very close to each other, giving p-CF_3 (K 0.674) > H (0.569) > m,m'-Cl_2 (0.554) > p-Br (0.546) > m-Cl (0.520) > p-Cl (0.509) > p-Me (0.492) > p-MeO (0.391). Apparently the equilibrium constants should not be used as a quantitative measure of the π-acceptor ability of the aryl groups, especially at higher temperatures, where the equilibrium is principally controlled by the entropy term.

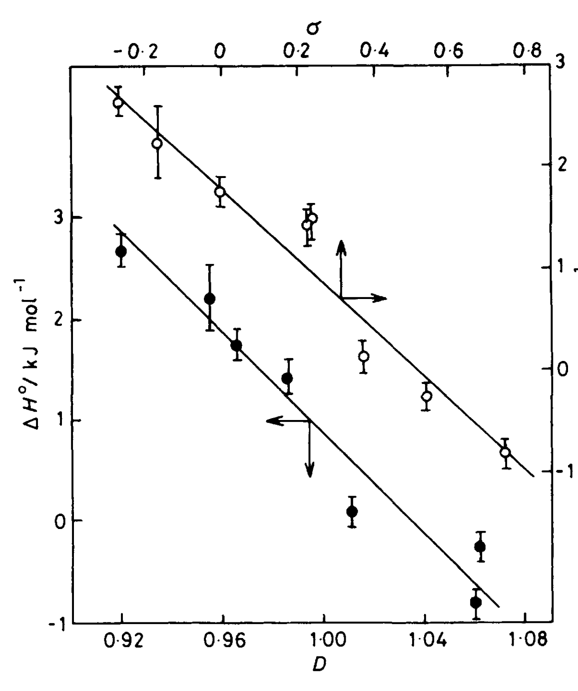

Figure 4. Plots of $\Delta H°$ values for the conversion of the CHT into the NCD form of 7-aryl-2,5-di-t-butylcyclohepta-1,3,5-trienes against D values and the Hammett σ-constants

Enthalpy and Entropy.—Because of the inadequacy of using the equilibrium constants of equation (3) as a measure of the π-acceptor ability of the aryl group, the $\Delta H°$ values were examined. Since the steric contribution of the *meta*- or *para*-substituent on the enthalpy difference between the CHT and the NCD tautomer can be regarded as negligibly small, the $\Delta H°$ values are considered to reflect only the electronic contributions of the substituents. Thus, a plot of $\Delta H°$ against the π-acceptor ability of the aryl groups as defined by the D values [equation (5)] affords a good linear relationship with $r = -0.9679$ for the case $-\varepsilon_\sigma - \lambda = 0.3$ (Figure 4).* A similar plot against the Hammett σ-constants also gives a good linear correlation with $r = -0.9701$ (Figure 4).†

The gradual decrease in $\Delta H°$ with increase in the π-acceptor ability (D) of the substituent can best be ascribed to increased electron donation from the Walsh orbital to the unoccupied πMOs of the aryl group. The stability of the CHT tautomer would be little affected by a change of the substituent, since the aryl group is not directly conjugated with the double bonds.

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* The $\Delta H°$ plot against D calculated for $-\varepsilon_\sigma - \lambda = 0.5$ gives a comparable linearity.

† Exclusion of the points for p-Cl and p-Br much improves the linearity ($r = -0.9961$).

The $\Delta S°$ values also exhibit a gradual decrease as the aryl group is made more electron-accepting. This might indicate that the degree of freedom of the aryl rotation decreases with increase in conjugative electron donation from the cyclopropane ring to the aryl group.

Evidence for Electron Donation.—Two pieces of evidence supporting electron donation from the cyclopropane ring to the aryl group may be obtained from the dependence of the chemical shifts of C(3), C(4), and the *para*-carbon atom of the aryl ring upon changing the substituent. First, the plots of the ^{13}C chemical shifts (in Hz) of C(3) and C(4) determined at 25.00 MHz and −117 °C against the Hammett σ-constants [23] are linear, with positive slopes in both the CHT ($r = 0.8579$) and the NCD tautomer ($r = 0.9965$). However, the slope with respect to the NCD tautomer ($\rho = 19.8$) is 4.3 times greater than that with respect to the CHT tautomer ($\rho = 4.6$). The result suggests that the conjugative electron donation is transmitted to the C(3) and C(4) positions in the NCD structure through conjugation between the C(2) or C(4) double bond and the cyclopropane ring [equation (3)], whereas only the inductive effect operates in the CHT structure.

Secondly, the *para*-carbon shift of the NCD tautomer is generally to higher field than that of the CHT tautomer. Specifically, the difference in the *para*-carbon shifts between the NCD and the CHT tautomer of the 7-phenyl system is 35 Hz (~3 169.0—3 133.5), whereas it is 46 Hz (~3 164.1—3 117.7) in the *m,m'*-dichlorophenyl system, suggesting that the *para*-carbon atom in the NCD tautomer of the latter system is more shielded relative to the CHT form than that in the NCD tautomer of the former system. This is ascribed to greater electron donation from the Walsh orbital to the aryl ring in the NCD tautomer in the *m,m'*-dichlorophenyl than in the phenyl case.

Experimental

Elemental analyses were performed by the Microanalytical Centre, Kyoto University. ^1H N.m.r. spectra at 35 °C were recorded by use of CCl_4 as solvent with a Hitachi R-24 (60 MHz) instrument. ^1H and ^{13}C n.m.r. spectra at various temperatures 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.

*7-Aryl-*2,5*-di-t-butylcyclohepta-*1,3,5*-trienes.*—All the compounds were prepared from the corresponding Grignard reagents and 1,4-di-t-butyltropylium perchlorate. In a typical example, to the Grignard reagent prepared from 1-bromo-4-trifluoromethylbenzene (0.302 g, 1.34 mmol) and Mg (0.038 g, 1.56 mmol) in anhydrous ether (4 ml) was added 1,4-di-t-butyltropylium perchlorate [19] over 2 min at 0 °C. After stirring at room temperature for 60 min, aq. NH_4Cl (15 ml) was added and then the mixture was extracted with ether. The ether layer was washed with 10% NaCl, dried ($MgSO_4$), and evaporated to afford yellowish crystals (0.204 g). Recrystallization from methanol gave pale yellow crystals (0.114 g) in 63% yield. M.p.s, ^1H n.m.r. data (*J* in Hz) (CCl_4; 35 °C), and elemental analyses for all the 7-aryl-2,5-di-t-butylcyclohepta-1,3,5-trienes are as follows: 7-(*p*-methoxyphenyl), m.p. 69.5—70.8 °C; δ 1.10 (18 H, s), 2.07 (1 H, t, *J* 5.0), 3.72 (3 H, s), 4.46 (2 H, d, *J* 5.0), 6.48 (2 H, s), 6.73 (2 H, d, *J* 9.0), and 7.10 (2 H, d, *J* 9.0) (Found: C, 84.9; H, 9.8. $C_{22}H_{30}O$ requires C, 85.1; H, 9.75%): 7-(*p*-methylphenyl), m.p. 99.5—100.0 °C; δ 1.12 (18 H, s), 2.03 (1 H, t, *J* 5.5), 2.33 (3 H, s), 4.33 (2 H, d, *J* 5.5), 6.44 (2 H, s), and 7.03 (4 H, s) (Found: C, 89.0; H, 10.4. $C_{22}H_{30}$ requires C, 89.75; H, 10.25%): 7-phenyl, m.p. 72.8—73.3 °C; δ 1.13 (18 H, s), 2.04 (1 H, t, *J* 5.5), 4.29 (2 H, d, *J* 5.5), 6.43 (2 H, s), and 7.16 (5 H, s) (Found: C, 90.1; H, 10.3. $C_{21}H_{28}$ requires C, 89.95; H, 10.05%): 7-(*p*-chlorophenyl), m.p. 94.0—95.0 °C; δ 1.13 (18 H, s), 2.07 (1 H, t, *J* 5.5), 4.35 (2 H, d, *J* 5.5), 6.50 (2 H, s), and 7.23 (4 H, br s) (Found: C, 79.9; H, 8.6. $C_{21}H_{27}Cl$ requires C, 80.1; H, 8.65%): 7-(*p*-bromophenyl),* m.p. 100.5—101.5 °C; δ 1.13 (18 H, s), 2.05 (1 H, t, *J* 5.5), 4.33 (2 H, d, *J* 5.5), 6.47 (2 H, s), 7.10 (2 H, d, *J* 9.0), and 7.40 (2 H, d, *J* 9.0) (Found: C, 71.8; H, 8.0; Br, 20.2. $C_{21}H_{27}Br$ requires C, 70.2; H, 7.55; Br, 22.25%): 7-(*m*-chlorophenyl), m.p. 62.5—64.0 °C; δ 1.12 (18 H, s), 2.09 (1 H, t, *J* 5.5), 4.33 (2 H, d, *J* 5.5), 6.47 (2 H, s), and 7.15 (4 H, br s) (Found: C, 80.0; H, 8.7. $C_{21}H_{27}Cl$ requires C, 80.1; H, 8.65%): 7-(*p*-trifluoromethylphenyl), m.p. 105.0—105.5 °C; δ 1.12 (18 H, s), 2.05 (1 H, t, *J* 5.5), 4.20 (2 H, d, *J* 5.5), 6.41 (2 H, s), 7.30 (2 H, d, *J* 8.0), and 7.55 (2 H, d, *J* 8.0) (Found: C, 75.8; H, 8.0. $C_{22}H_{27}F_3$ requires C, 75.85; H, 7.8%): 7-(*m,m'*-dichlorophenyl), m.p. 84.5—86.0 °C; δ 1.10 (18 H, s), 2.07 (1 H, t, *J* 5.0), 4.38 (2 H, d, *J* 5.0), 6.48 (2 H, s), 7.07 (2 H, d, *J* 1.2), and 7.18 (1 H, t, *J* 1.2) (Found: C, 72.2; H, 7.7. $C_{21}H_{26}Cl_2$ requires C, 72.2; H, 7.5%).

Variable-temperature ^{13}C *N.m.r. Spectra.*—The measurements were conducted on a solution (2 ml) of the 7-aryl-2,5-di-t-butylcyclohepta-1,3,5-triene (0.15M) 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 Me_4Si scale using δ(CS_2) 192.24. Generally the spectra were obtained employing a 5 000 Hz width in 8 192 data points by use of a 45° pulse, pulse repetition of 1.5 s, and 384 pulses. The temperature indicator was calibrated to within ±1 °C by using CCl_4–$(CD_3)_2CO$ as an n.m.r. thermometer.[26]

Variable-temperature ^1H *N.m.r. Spectra.*—The measurements were conducted on a solution (0.4 ml) of 7-phenyl-2,5-di-t-butylcyclohepta-1,3,5-triene (0.08M) dissolved in CS_2–CD_2Cl_2 (3 : 1 v/v) containing Me_4Si, in a 5 mm cell. Generally the spectra were obtained employing a 1 000 Hz width in 16 384 data points by use of a 50° pulse, pulse repetition of 8 s, and 16 pulses. The temperature indicator was calibrated to within ±1 °C by using methanol containing 0.03% concentrated hydrochloric acid as an n.m.r. thermometer.[27]

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* This compound was contaminated by 8% of 1,4-bis-(2,5-di-t-butylcyclohepta-1,3,5-trien-7-yl)benzene, which could not be separated by recrystallization, h.p.l.c., or t.l.c. However, no difficulty has been experienced in determining equilibrium constants in its presence.

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