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# PRIMARY DEPENDENCE OF 7-ARYL-2,5-DI-t-BUTYL-1,3,5-CYCLOHEPTATRIENE VALENCE TAUTOMERISM ON THE π-ACCEPTOR STRENGTH OF THE 7-ARYL SUBSTITUENT

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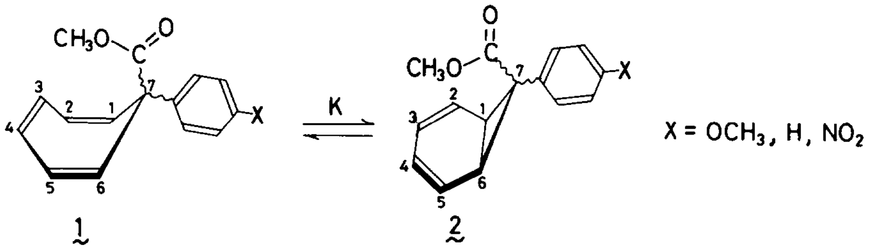
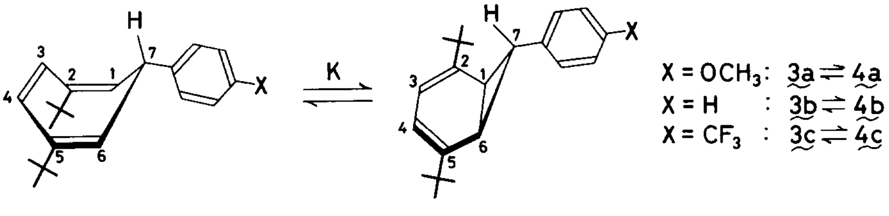
Abstract. $^{13}C$ NMR studies showed that the population of the norcaradiene form of the title systems containing p-$CH_3O$, H, and p-$CF_3$ on the 7-aryl group increases in this order. The result is consistent with the prediction from the π-acceptor strength of the aryl group estimated by INDO calculations.

Various factors affect cycloheptatriene (CHT) - norcaradiene (NCD) equilibria.[1] Among those the remarkable effects of electron-withdrawing substituents such as CN, COOH, or CHO at the 7-position to favor the NCD form have been ascribed by Hoffmann[2a] and Gunther[2b] to electron donation from the Walsh orbital of the cyclopropane ring in the NCD form toward low-lying unoccupied π-MO of the substituent. Because the orbital is antibonding between C(1) and C(6), this electron delocalization has been interpreted to strengthen the C(1)-C(6) bond.[2] On the other hand, the complicating effects of aryl substituents on the equilibrium ($1 \rightleftharpoons 2$) reported by Hall and Roberts[3] have been interpreted to render the above theory untenable in a general way:[4] the equilibrium constant increases in the order H < $NO_2$ < $OCH_3$ at below 32.5°C, whereas the order is reversed at above 75°C.[3] Thus either order is incompatible with the order $OCH_3$ < H < $NO_2$ predicted from the increasing order of the π-acceptor strength of the aryl group.[1a,4] Later, Gunther and his coworkers showed that the system $1 \rightleftharpoons 2$ is unsuitable for examining the above theory because the aryl group in 2 is actually oriented endo and assumes an unfavorable conformation for electron acceptance from the cyclopropane ring, with the $2p_z$-orbital being orthogonal to the Walsh orbital.[5] Unfortunately, the existence of 7-phenyl-1,3,5-cycloheptatriene essentially in the CHT form[6] prevented examination of the exo-aryl substituent effect in the parent system where the aryl group can assume a favorable conformation for electron acceptance.



Previously we reported that the introduction of two t-butyl groups to the 2- and 5-positions of 7-t-butyl-7-cyano-1,3,5-cycloheptatriene enormously shifts the equilibrium to the NCD form.[7] Here we wish to report that the application of this technique to 7-aryl-1,3,5-

cycloheptatriene (3a ⇌ 4a, 3b ⇌ 4b, 3c ⇌ 4c) brings the population of the NCD form (4) to approximately 30% at 25°C, thereby permitting determination of the equilibrium constants by $^{13}C$ NMR. The most important conclusion reached is that the NCD form is stabilized in the order $OCH_3 < H < CF_3$, which is consistent with the increasing order of the π-acceptor strength of the aryl group predicted from INDO calculations.



3 4

The three equilibrating systems (3 ⇌ 4) were prepared by treating 1,4-di-t-butyltropylium perchlorate[7] with the corresponding aryl Grignard reagents, and the products purified by recrystallization or HPLC. The $^{13}C$ NMR spectra were measured in $CS_2$-$CD_2Cl_2$ (3:1 in vol.) at 25° and -112°C. Pertinent spectral data are summarized in Table 1, and the spectra for 3b ⇌ 4b are shown in the Figure as a representative example. At 25°C, only time averaged signals are observed, whereas at -112°C each signal splits into two, each of which corresponds to either of 3b or 4b.[8,9] No indication for the existence of conformational or configurational isomers other than 3 or 4 has been obtained, as evident in the $^{13}C$ NMR spectra (Fig.). The equilibrium constants for 3 ⇌ 4 at 25°C were calculated by applying the equation $K = (\delta_{CHT} - \delta)/(\delta - \delta_{NCD})$ to the C(1,6), C(3,4), and C(7) signals, whereas those for 3 ⇌ 4 at -112°C were determined by measuring signal intensities for five CHT - NCD signal pairs which were selected from the six

Table 1. $^{13}C$ NMR (25 MHz) chemical shifts (δ) for 3 ⇌ 4 systems at 25° and -112°C.[a]

| X | Temp./°C | Structure | C(1,6) | C(2,5) | C(3,4) | C(7) | $(\underline{C}H_3)_3C$ | $(CH_3)_3\underline{C}$ |
|---|---|---|---|---|---|---|---|---|
| $OCH_3$[b] | 25 | 3a ⇌ 4a | 100.14 | 143.51 | 126.21 | 38.74 | 29.63 | 34.21 |
| | -112 | 3a | 124.39 | 142.61 | 130.86 | 44.23 | 29.75 | 34.09 |
| | -112 | 4a | 31.17 | 144.95 | 112.25 | 23.17 | 28.39 | 35.16 |
| H[c] | 25 | 3b ⇌ 4b | 93.50 | 143.80 | 124.95 | 38.11 | 29.43 | 34.26 |
| | -112 | 3b | 124.19 | 142.86 | 130.92 | 45.20 | 29.80 | 34.19 |
| | -112 | 4b | 31.95 | 145.15 | 112.54 | 24.00 | 28.39 | 35.26 |
| $CF_3$[d] | 25 | 3c ⇌ 4c | 86.74 | 144.38 | 124.07 | 36.74 | 29.38 | 34.45 |
| | -112 | 3c | 123.17 | 143.34 | 131.01 | 45.10 | 29.70 | 34.19 |
| | -112 | 4c | 33.02 | 145.05 | 112.99 | 24.30 | 28.34 | 35.26 |

(a) The chemical shifts from TMS were calculated on the basis of the δ-value of $CD_2Cl_2$ (53.11 at 25° and 54.21 at -112°C) in $CS_2$-$CD_2Cl_2$ (3:1 in vol.). The concentrations were 0.072 M for 3a ⇌ 4a, 0.14 M for 3b ⇌ 4b, and 0.17 M for 3c ⇌ 4c. The spectra were recorded on a JEOL JNM FX100 at a spectral width of 5000 Hz by use of a 45° pulse and a pulse repetition of 1.5 s. (b) Mp 69.5 - 71.5°C. (c) Mp 73.0 - 74.0°C. (d) Mp 105.0 - 105.5°C.

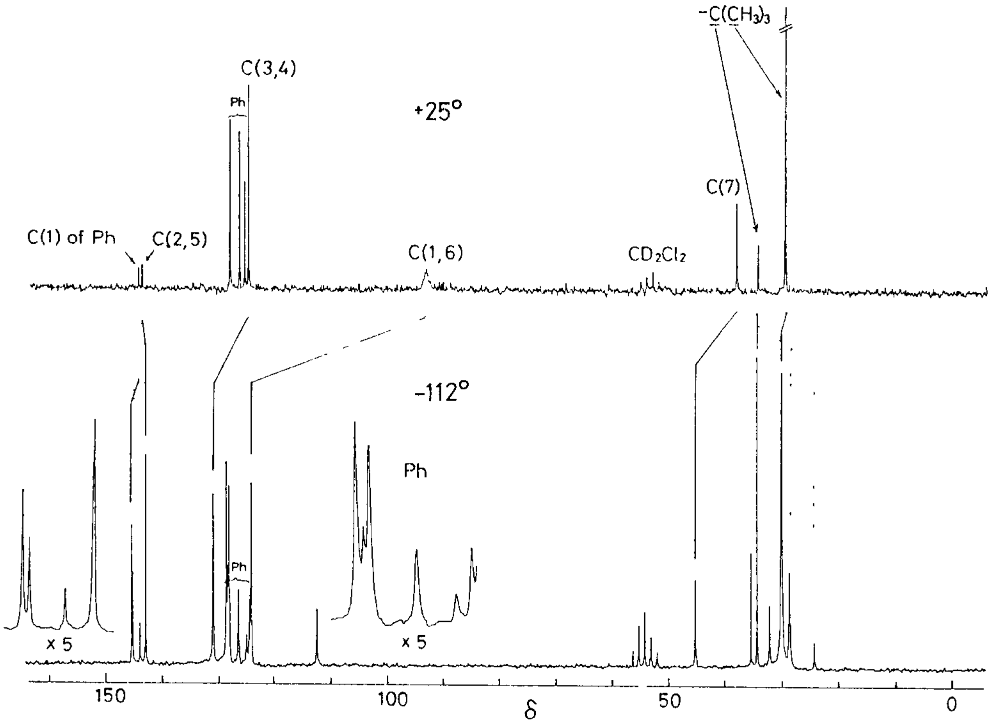


Figure. $^{13}$C NMR (25 MHz) spectra for the **3b** $\rightleftharpoons$ **4b** system in $CS_2$-$CD_2Cl_2$ (3:1 in vol.) at 25° and -112°C. The solid and the dotted lines represent the signals assigned to **3b** and **4b**, respectively. For measurement conditions see the footnote of Table 1.

Table 2. Populations, equilibrium constants, and thermodynamic parameters for **3** $\rightleftharpoons$ **4** systems.

| X | Temp./°C | Population/%[a] 3 | Population/%[a] 4 | K | ΔH°/kJ $mol^{-1}$ | ΔS°/J $K^{-1}mol^{-1}$ |
|---|---|---|---|---|---|---|
| $OCH_3$ | 25 | 74.3±0.6 | 25.7±0.6 | 0.346 | +3.19 | +1.9 |
| | -112 | 89.6±0.6 | 10.4±0.6 | 0.116 | | |
| H | 25 | 66.9±0.5 | 33.1±0.5 | 0.495 | +1.13 | -2.5 |
| | -112 | 74.9±1.2 | 25.1±1.2 | 0.335 | | |
| $CF_3$ | 25 | 60.3±1.0 | 39.7±1.0 | 0.658 | -0.46 | -5.0 |
| | -112 | 56.5±0.8 | 43.5±0.8 | 0.770 | | |

(a) For calculation see text.

pairs listed in Table 1. The results are summarized in Table 2 along with thermodynamic parameters. At either temperature the equilibrium constant increases in the order $OCH_3$ < H < $CF_3$.

Three extended lines of the customary plot of ln K values at 25° and -112°C vs. 1/T cros at the point corresponding to 253°C, suggesting that the order of the equilibrium constant is reversed to $CF_3$ < H < $OCH_3$ at the higher temperatures provided that the plot is linear over such a wide temperature range. However, at lower temperatures, where the equilibrium is principally controlled by ΔH°, the stability of the NCD form **4** follows the order predicted from the π-acceptor strength of the aryl group which is evaluated by INDO calculations as below.

The ability of the pπ atomic orbital $\chi_r$ in an aryl fragment for electron acceptance is estimated by $\Sigma_j^{uno} c_{jr}^2/(\varepsilon_j - \varepsilon_\sigma - \lambda)$,[11] where $c_{jr}$ is the coefficient of the atomic orbital in the unoccupied π-MO $\Phi_j$, $\varepsilon_j$ and $\varepsilon_\sigma$ denote energies of the aryl π-MO and the antisymmetric occupied Walsh orbital of cyclopropane ring, respectively, and λ stands for the repulsion between a pair of electrons populated in these MO's. $\varepsilon_\sigma$ is suggested to be in the range -0.5 ∿ -0.6 (-0.527 in the case of cyclopropane) and λ is evaluated to be 0.1 ∿ 0.2 in atomic unit. Summing up the quantity over all the unoccupied π-MO's of the aryl fragment, an INDO SCF MO calculation yielded 0.731, 0.690 and 0.654 for $\phi$-$CF_3$, $\phi$-H and $\phi$-$OCH_3$ in the case of $-\varepsilon_\sigma - \lambda = 0.5$, and 1.034, 0.958 and 0.902 in the case of $-\varepsilon_\sigma - \lambda = 0.3$, with regard to the ary carbon atom which is located adjacent to C(7). This result is consistent with the experimenta results and supports the notion of Hoffmann[2a] and of Günther[2b].

## References and notes

1. a) W. J. le Noble, "Highlights of Organic Chemistry", Marcel Dekker, Inc., New York, 1974, p. 402; b) K. Takahashi, K. Takase, and H. Toda, Chem. Lett., 979 (1981), and references cited therein.
2. a) R. Hoffmann, Tetrahedron Lett., 2907 (1970); b) H. Günther, ibid., 5173 (1970).
3. G. E. Hall and J. D. Roberts, J. Amer. Chem. Soc., 93, 2203 (1971).
4. T. H. Lowry and K. S. Richardson, "Mechanism and Theory in Organic Chemistry", Harper & Row, Publishers, New York, 1976, p. 654.
5. H. Günther, W. Peters, and R. Wehner, Chem. Ber., 106, 3683 (1973).
6. a) H. Günther, M. Gorlitz, and H.-H. Hinrichs, Tetrahedron, 24, 5665 (1968); b) R. W. Murray and M. L. Kaplan, J. Amer. Chem. Soc., 88, 3527 (1966); c) A. P. ter Borg and H. Kloosterziel, Recl. Trav. Chim. Pays-Bas, 82, 741 (1963).
7. K. Takeuchi, M. Arima, and K. Okamoto, Tetrahedron Lett., 22, 3081 (1981).
8. All the signals were assigned with the aid of $^1H$ NMR and off-resonance $^{13}C$ NMR spectra: the details will be presented elsewhere.
9. The $^1H$ NMR spectrum of the **3b** $\rightleftharpoons$ **4b** system in $CS_2$-$CD_2Cl_2$ (3:1 in vol.) at -110°C exhibits H(7) of **3b** at δ 2.49 (t, J=5.6 Hz). This δ-value agrees well with δ 2.68[6a] for H(7) of 7-phenyl-1,3,5-cycloheptatriene, in which H(7) is known to assume axial conformation.[6] In the same spectrum H(7) of **4b** appears at δ 0.80 (t, J=4.0 Hz). This upfield shift of H(7) of the NCD form as compared with δ 1.71[10] for H(1) of cyclopropylbenzene indicates the endo configuration of H(7). The coupling constant (4.0 Hz) which is comparable to $J_{trans}$ = 6.30[10] rather than $J_{cis}$ = 9.45 Hz[10] of cyclopropylbenzene also substantiates the configuration of **4b**.
10. J. Bacon, R. J. Gillespie, and K. C. Westaway, cited in W. Brügel, "Handbook of NMR Spectral Parameters", Vol. 1, Heyden & Sons, Ltd., London, 1979, p. 251.
11. K. Fukui and H. Fujimoto, Bull. Chem. Soc. Jpn., 41, 1989 (1968).

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