Determination of Subtle Differences in π-Acceptor Ability of Ethynyl, Cyano, and Phenylethynyl Groups using the Cycloheptatriene–Norcaradiene Equilibrium in 7-Substituted 2,5-Di-t-butylcyclohepta-1,3,5-trienes[1]

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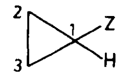
The equilibrium constant {K = [norcaradiene]/[cycloheptatriene]} determined by ^{1}H n.m.r. spectroscopy of the title system with the substituent in the *exo* or equatorial position are 0.213 ± 0.002, 0.258 ± 0.002, and 0.374 ± 0.004 for ethynyl, cyano, and phenylethynyl, respectively, in CS_2–CD_2Cl_2 (3 : 1 v/v) at −120 °C, which indicate an increasing π-acceptor ability towards the cyclopropane ring which follows this order of the substituents.

Orbital theory suggests that the cyclopropane ring behaves as an electron donor towards π-acceptor substituents, which causes a shortening of the C(2)–C(3) bond and lengthening of the C(1)–C(2) and C(1)–C(3) bonds.[2] This has been supported by *X*-ray[3] and microwave[4] studies. However, the detection of a subtle difference in the π-acceptor abilities of different Z groups appears to be difficult in geometric studies because of inherent experimental uncertainties. A recent microwave study on cyclopropanecarbonitrile and cyclopropylacetylene showed that in the former the C(2)–C(3) bond was shorter by 0.002 Å and the C(1)–C(2) bond longer by 0.003 Å than the corresponding bonds in the latter.[4] Although the results were in accord with the prediction that the cyano group would be a better acceptor than the ethynyl group, the experimental uncertainties (0.003—0.007 Å) were too large to provide definite proof.[4]

On the other hand, the equilibrium constants (or $\Delta H°$ values) for the valence tautomerism between 7-substituted cyclohepta-1,3,5-trienes (CHT's) and bicyclo[4.1.0]hepta-2,4-dienes (norcaradienes; NCD's) can be determined by variable-temperature ^{1}H n.m.r. spectroscopy with good precision and permit the evaluation of the relative π-acceptor abilities of the substituents.[5,6] As the acceptor ability increases, the position of equilibrium shifts to the NCD side.

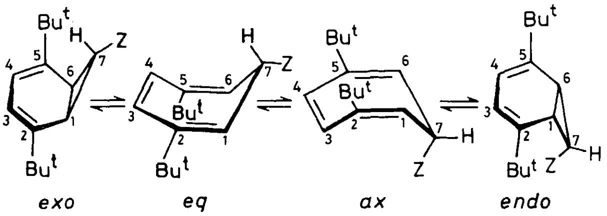
We have previously succeeded in determining the populations of the four tautomers of 7-cyano-2,5-di-t-butylcyclohepta-1,3,5-triene (**1**) by ^{1}H n.m.r. spectroscopy at −120 °C [equation (1)] (*eq* = equatorial, *ax* = axial),[7] although without the t-butyl groups no NCD tautomers have been detected.[5a,8] We now report the CHT–NCD equilibrium constants for 7-ethynyl- and 7-(phenylethynyl)-2,5-di-t-butylcyclohepta-1,3,5-trienes (**2**) and (**3**), respectively, with the substituent in the *eq* or *exo* position, at −120 °C in CS_2–CD_2Cl_2 (3 : 1 v/v). Comparison of the data with the value for (**1**) provides the first definite determination of subtle differences among the relative π-acceptor abilities of the three Z groups.



Z = π-acceptor substituent

The compounds (**2**) (unstable liquids) and (**3**) (m.p. 74.0—76.0 °C) were prepared in *ca.* 17% yield by treatment of 1,4-di-t-butyltropylium perchlorate[9] with ethynyl- and phenylethynyl-lithium, respectively, in tetrahydrofuran at −30 °C, followed by separation from other isomers by h.p.l.c. (Waters μ-Porasil column; hexane); satisfactory elemental analyses were obtained. The ^{1}H n.m.r. data are summarized in Table 1. The assignments of signals are based on the previously reported spectra of (**1**).[7] The coalesced signals at 24 °C split at low temperatures into two major ones assigned to *exo*-NCD [(**2**-*exo*) or (**3**-*exo*)] and *eq*-CHT [(**2**-*eq*) or (**3**-*eq*)]. Existence of *endo*-NCD [(**2**-*endo*) or (**3**-*endo*)] was indicated by the weak singlet of H(3,4) at δ *ca.* 5.7. No signals for H(7) of (**2**-*ax*) or (**3**-*ax*) were observed in the range of δ 2.5—5.2.

In the two pairs of structures in the CHT–NCD equilibrium [equation (1)], the equilibrium between the *ax* and *endo* tautomer is markedly affected by the through-space interactions of the substituent on C(7) with C(3) and C(4), whereas



(1)

(**1**); Z = N≡C–
(**2**); Z = HC≡C–
(**3**); Z = PhC≡C–

Table 1. 99.55 MHz ^{1}H Fourier transform n.m.r. data for (**2**) and (**3**) in CS_2–CD_2Cl_2 (3 : 1 v/v), [(**2**)] = 0.090 M; [(**3**)] = 0.15 M.[a]

Temp./°C	Tautomer	Chemical shift (δ) H(1,6)	H(3,4)	H(7)	Bu^t	$J_{1,7}$ (= $J_{6,7}$) /Hz	Population/%[b] at −120 °C
24	(**2**)[c]	4.36(d)	6.40(s)	1.84(dt)[e]	1.08(s)	5.7	—
−120	(**2**-*exo*)	2.18(d)	5.50(s)	0.27(br.)	1.14(s)	3.9	16.9 ± 0.1
−120	(**2**-*eq*)[d]	5.20(d)	6.75(s)	2.2(br.)[f]	1.06(s)	5.7	79.5 ± 0.3
−120	(**2**-*endo*)	—[g]	5.69(s)	—[g]	—[g]	—[g]	3.6 ± 0.2
24	(**3**)[c]	4.32(d)	6.38(s)	2.00(t)	1.11(s)	5.7	—
−120	(**3**-*exo*)	2.33(d)	5.53(s)	0.50(t)	1.15(s)	3.9	26.4 ± 0.2
−120	(**3**-*eq*)[d]	5.30(d)	6.78(s)	2.47(t)	1.09(s)	5.7	70.6 ± 0.2
−120	(**3**-*endo*)	—[g]	5.76(s)	—[g]	—[g]	—[g]	3.0 ± 0.1

[a] Aryl and ethynyl protons are not shown. [b] Determined by the integration of H(3,4) signals. [c] All signals are coalesced. [d] The axial tautomer has not been detected (<1%). [e] J with ethynyl proton is 2.3 Hz. [f] Overlapped with the H(1,6) signal of (**2**-*exo*). [g] The signal could not be detected because of low intensity or overlapping with other signals.

the equilibrium between the *eq* and the *exo* tautomer is free from such steric factors.[5,7,8b] Therefore, for evaluating the relative π-acceptor abilities of the substituents, the equilibrium constants between the *eq*-CHT and the *exo*-NCD tautomers should be employed.†[5] The populations in Table 1, which were determined by integrating the H(3,4) signals, afford [(**2**-*exo*)]/[(**2**-*eq*)] = 0.213 ± 0.002 and [(**3**-*exo*)]/[(**3**-*eq*)] = 0.374 ± 0.004 at -120 °C. Carefully repeated integrations of the spectrum of (**1**) measured under the same conditions afforded [(**1**-*exo*)]/[(**1**-*eq*)] = 0.258 ± 0.002.‡ Consequently, the π-acceptor ability increases in the order: ethynyl < cyano < phenylethynyl. Thus, the present system [equation (1)] is a promising tool for evaluating the relative π-acceptor abilities of various substituents.

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† For strict comparisons, ΔH° values should be determined. However, (**1**)—(**3**) contain substituents of similar cylindrical shape and would show similar ΔS° values, which permits the use of the equilibrium constants at low temperatures as a measure of the π-acceptor ability.

‡ For the ^{1}H n.m.r. data see ref. 7. Newly determined populations are 15.8 ± 0.1 (**1**-*exo*), 61.1 ± 0.1 (**1**-*eq*), 2.1 ± 0.1 (**1**-*ax*), and 21.0 ± 0.1% (**1**-*endo*).

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