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DYNAMIC BEHAVIOUR IN (1′-t-BUTYL-2′,2′-DIMETHYLPROPYL)-π-(TRICARBONYLCHROMIUM)BENZENE

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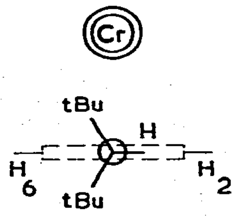
Summary

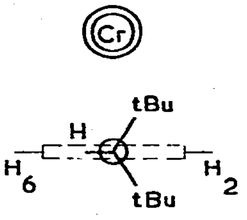
The temperature dependence of the ^{1}H NMR spectrum of the title compound was studied over the temperature range 0—115°C. Two conformers were detected. The conformational isomerism is caused by a restricted rotation about the bond between the alkyl group and the complexed aromatic ring. The $\Delta G^\ddagger$ value for the interconversion amounts to 16.9 kcal mol^{-1}, which is substantially smaller than the corresponding $\Delta G^\ddagger$ value for the free ligand. This decrease is ascribed to additional steric strain between the alkyl and the tricarbonylchromium groups in the conformers of the complex.

Introduction

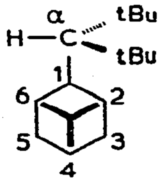
In a previous paper [1] we described the ^{1}H NMR spectra of (1′-t-butyl-2′,2′-dimethylpropyl)-π-(tricarbonylchromium)benzene and the corresponding free ligand. In both compounds the two *ortho* (and *meta*) protons are inequivalent at room temperature. Equivalence can be obtained dynamically by a rapid interconversion of the conformers I and II. In an earlier study on some 3,4-disubstituted (1′-t-butyl-2′,2′-dimethylpropyl)benzenes [2] the barrier to rotation about the C_1—C_α single bond was determined at 22 kcal mol^{-1}.



I



II



III

Recently, we have determined the molecular geometry of (1′-t-butyl-2′,2′-dimethylpropyl)-π-(tricarbonylchromium)benzene [3]. Since the molecule possesses no strain-free conformations, it seemed worthwhile to determine the influence of steric interactions between the CH-t-Bu_2 group and the $Cr(CO)_3$ group upon the barrier to rotation about the C_1—C_α bond in the complex. This paper presents a study of the temperature dependence (0—115°C) of the ^1H NMR spectra of the title compound.

Results and discussion

^1H NMR spectra of the compound, dissolved in tetrachloroethene containing cyclosilane as internal standard, were recorded on a Varian XL-100-15 spectrometer equipped with a variable temperature accessory.

Spectra of (1′-t-butyl-2′,2′-dimethylpropyl)-π-(tricarbonylchromium)benzene at 0 and 115°C are shown in Fig. 1. The assignment of the signals of the aromatic protons follows that given earlier [2]. This assignment was based on steric overcrowding [4], which may cause hindering of solvation [5]. The behaviour shown in the spectra points to the presence of two rotamers about C_1—C_α, I and II,

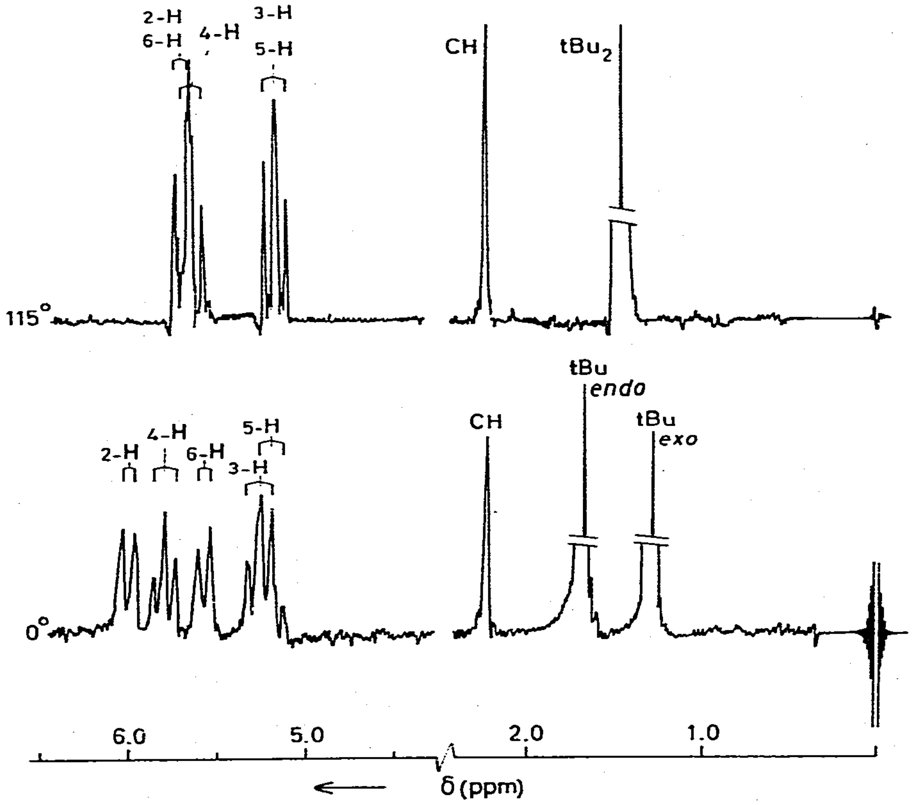


Fig. 1. ^1H NMR spectra of (1′-t-butyl-2′,2′-dimethylpropyl)-π-(tricarbonylchromium)benzene (numbering according to formula III).

TABLE 1

COALESCENCE TEMPERATURES, FREQUENCY DIFFERENCES AND FREE ENERGIES OF ACTIVATION FOR THE CONFORMERS OF (1′-t-BUTYL-2′,2′-DIMETHYLPROPYL)-π-(TRICARBONYLCHROMIUM)BENZENE IN TETRACHLOROETHENE

(standard deviations in parentheses)

	Aromatic protons		t-Bu protons
	2 6	3 5	
T_c (°C)	74(3)	58(3)	66(1)
$\Delta\nu^a$ (Hz)	42(1)	8(1)	38.6(0.5)
$\Delta G^{\ddagger}$ at T_c (kcal mol^{-1})	17.3(0.4)	17.5(0.4)	16.9(0.2)

[a] Extrapolated to the coalescence temperature.

which exchange slowly at 0° C. At higher temperatures the exchange rate increases and the signals of the aromatic protons coalesce to an *AA′BXX′* pattern. Moreover, the two signals of the protons of the t-Bu groups coalesce to a single line. The coalescence temperatures and the barriers to rotation, which have been calculated using the simplified formulas [6] with a transmission coefficient of 1, are given in Table 1.

The most accurate value of $\Delta G^{\ddagger}_{339}$ (16.9 kcal mol^{-1}) is obtained from the coalescence of the t-Bu signals. The barrier to rotation about the C_1—C_α bond in (1′-t-butyl-2′,2′-dimethylpropyl)-π-(tricarbonylchromium)benzene is substantially lower than the corresponding one in the free ligand ($\Delta G^{\ddagger}_{431}$ 22.2 kcal mol^{-1} [2]). A comparison of the molecular structures of the title compound [3] and 1-(4-methoxyphenyl)-2,2,6,6-tetramethylcyclohexanol [7], which resembles the free ligand, gives confidence that the geometry around the C_1—C_α bond is similar, with the exception that in the complex C_α is forced, by 0.41 Å, out of the aromatic plane away from the $Cr(CO)_3$ group [3]. The exchange between conformers I and II via a clockwise rotation of the CH-t-Bu$_2$ group about the C_1—C_α bond in I (or an anti clockwise rotation in II) seems highly improbable because of the very unfavourable interactions between the t-Bu groups and the $Cr(CO)_3$ group on the same side of the ring, which should occur in the transition state of this rotation. Therefore, the conversion of conformer I into conformer II is restricted to an anti clockwise rotation (in I). In this transition state the interaction between the alkyl and the $Cr(CO)_3$ groups is negligible. The decrease of the barrier to rotation about the C_1—C_α bond in the complex as compared with the free ligand is ascribed to a relief of steric strain between these two groups in this transition state. Thus, the strain present in the initial state (conformers I and II) of the complex must be about 5 kcal mol^{-1} larger than in the free ligand *.

Acknowledgements

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* It should be noted, however, that the two possible pathways for interconversion have equal probabilities in the free ligand, but not in the complex; for the comparison, the $\Delta G^{\ddagger}$ value obtained for the complex is expected to be increased by 0.5 kcal mol^{-1} due to a statistical factor in $\Delta S^{\ddagger}$ [8].

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References

1 F. van Meurs, J.M. van der Toorn and H. van Bekkum, J. Organometal. Chem., 113 (1976) 341.
2 J.M.A. Baas, Rec. Trav. Chim. Pays-Bas, 91 (1972) 1287.
3 F. van Meurs and H. van Koningsveld, J. Organometal. Chem., 118 (1976) 295.
4 F.A. Bovey, F.P. Hood, E. Pier and H.E. Weaver, J. Amer. Chem. Soc., 87 (1965) 2060.
5 D.H. Williams, J. Ronayne and R.G. Wilson, Chem. Commun., (1967) 1089.
6 J.A. Pople, W.G. Scheider and H.J. Bernstein, High-resolution Nuclear Magnetic Resonance, McGraw-Hill, New York, 1959, p. 223; R.J. Kurland, M.B. Rubin and M.B. Wise, J. Chem. Phys., 40 (1964) 2426; cf. D. Kost, E.H. Carlson and M. Raban, Chem. Commun., (1971) 656.
7 H. van Koningsveld, Cryst. Struct. Commun., 3 (1973) 491.
8 A.J.M. Reuvers, A. Sinnema, Th.J. Nieuwstad, F. van Rantwijk and H. van Bekkum, Tetrahedron, 27 (1971) 3713.