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INVESTIGATION OF ROTATIONAL ISOMERIZATION OF 6-DIMETHYLAMINOFULVENTRICARBONYL-CHROMIUM, -MOLYBDENUM AND -TUNGSTEN BY DYNAMIC ^{1}H NMR SPECTROSCOPY

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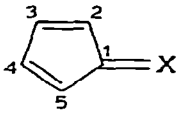
Summary

^{1}H NMR spectroscopy was used in studying the rotational isomerism of 6-dimethylaminofulvene and its complexes with carbonyls of chromium, molybdenum and tungsten. The energy parameters for the barriers to rotation about the C(6)—N bond were determined. It is shown that the coordination of 6-dimethylaminofulvene with Group VIB metal carbonyls increases the free energy for the barrier to rotation about the C(6)—N bond, that is, it increases the degree of double-bond character between the C(6) and N atoms. The free energy for the rotational barriers, and hence, the degree of double-bond character, are strongly dependent on the nature of the central metal atom, increasing in the sequence W < Mo < Cr. Also studied was the effect of the solvent on variations in the free energy for the rotational barrier. It was established that the increasing solvent polarity in the sequence acetone < nitromethane < dimethylformamide raises the rotational barrier, and hence, increases the C(6)—N bond order.

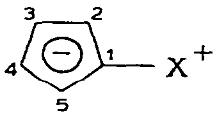
Introduction

The effect of complexing on the structure and reactivity of the initial organic compounds used as π-ligands is among the most challenging problems of the chemistry of π-complexes of transition metals. Convenient models for solving this problem include π-complexes of transition metal carbonyls with pentafulvenes (I) and cyclopentadienylides (II). Such a choice is prompted by the chemical properties of fulvenes, which are typical of classical polyenes on the one band and aromatic compounds on the other [1].

It is known that the properties of fulvenes are to a great extent dependent



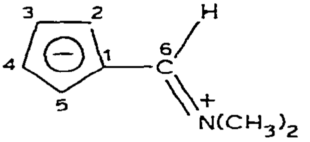
(I, X = CR_2)



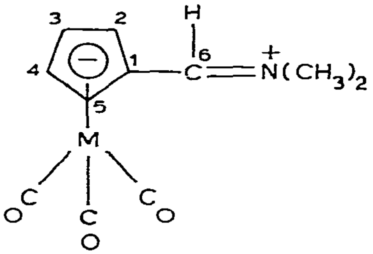
(II, X = SR_2, PR_3, $CHNR_2$)

on the degree of double-bond character between the C(1) and X atoms [2]. Therefore, we considered it important to find out how the complexing of such compounds with transition metal carbonyls affects the degree of the above-mentioned double-bond character, and in what way it is related to the nature of the central metal atom.

So far there are no answers to these questions, because it is difficult to evaluate the degree of double-bond character between the C(1) and X atoms for most pentafulvenes and cyclopentadienylides. However, such evaluation is possible in some cases, particularly in the case of 6-dimethylaminofulvene (III) and its complexes with Group VIB metal carbonyls (IV—VI).



(III)



(IV, M = Cr, V, M = Mo; VI, M = W)

The degree of double-bond character between the C(1) and C(6) atoms of these compounds is so related to that between the C(6) and N atoms that as the C(1)—C(6) bond order increases, that of the C(6)—N bond decreases, and vice versa. Therefore, one of the possible approaches to solve this problem may be a study of the rotational isomerisation about the C(6)—N bond of these compounds by dynamic ^1H NMR spectroscopy, along with a determination of the energy parameters for this process, since a change in the free energy for the rotational barrier is related to a change in the degree of double-bond character between the C(6) and N atoms, as follows: the higher the rotational barrier, the greater the C(6)—N bond order, the positive charge at the —HC(6)—$N(CH_3)_2$ group, the electron density at the cyclopentadienyl ring, and, hence, the polarity of the fulvene fragment.

In this paper we report a study of the rotational isomerism of 6-dimethylaminofulventricarbonyl-chromium (IV), -molybdenum (V) and -tungsten (VI) by dynamic ^1H NMR spectroscopy, using solvents of different polarity, and compare the energy parameters found for C(6)—N rotational barriers of these complexes with the corresponding energy parameters for the parent fulvene III.

Results and discussion

The temperature-dependence of the ^1H NMR spectra of 6-dimethylaminofulventricarbonyl-chromium (IV), -molybdenum (V) and -tungsten (VI) was studied over the temperature range —65 to 61°C, in acetone, nitromethane and

TABLE 1

^1H CHEMICAL SHIFTS OF COMPLEXES IV—VI IN ACETONE (δ, ppm FROM TMS)

Complex	Temperature (°C)	H(2)	H(5)	H(3)	H(4)	H(6)	CH_3
IV	−60	5.50	5.22	4.94 [a]		8.02	3.51, 3.31
V	−65	6.06	5.52	5.61	5.40	8.21	3.51, 3.29
VI	−50	5.96	5.54	5.37		8.18	3.24, 3.06

[a] Chemical shift of the signal belonging to H(3) and H(4); signal intensity ratio H(2)/H(5)/H(3) + H(4) = 1/1/2.

dimethylformamide (DMF). Since no values of $\Delta G^{\ddagger}$ for the barrier to rotation about the C(6)—N bond in 6-dimethylaminofulvene (III) in the solvents involved are available in the literature, we also studied the temperature-dependence of the ^1H NMR spectra of III in acetone.

The ^1H NMR spectral parameters of complexes IV—VI are shown in Table 1. The ^1H NMR spectra recorded at various temperatures for the protons in the cyclopentadienyl ring and methyl groups of compounds IV—VI are shown in Figs. 1 and 2, respectively.

Analysis of the data obtained showed that a change in temperature brought about reversible changes in the number and shape of signals from the protons of the cyclopentadienyl ring and methyl groups.

The energy parameters for the barriers restricting the rotation about the

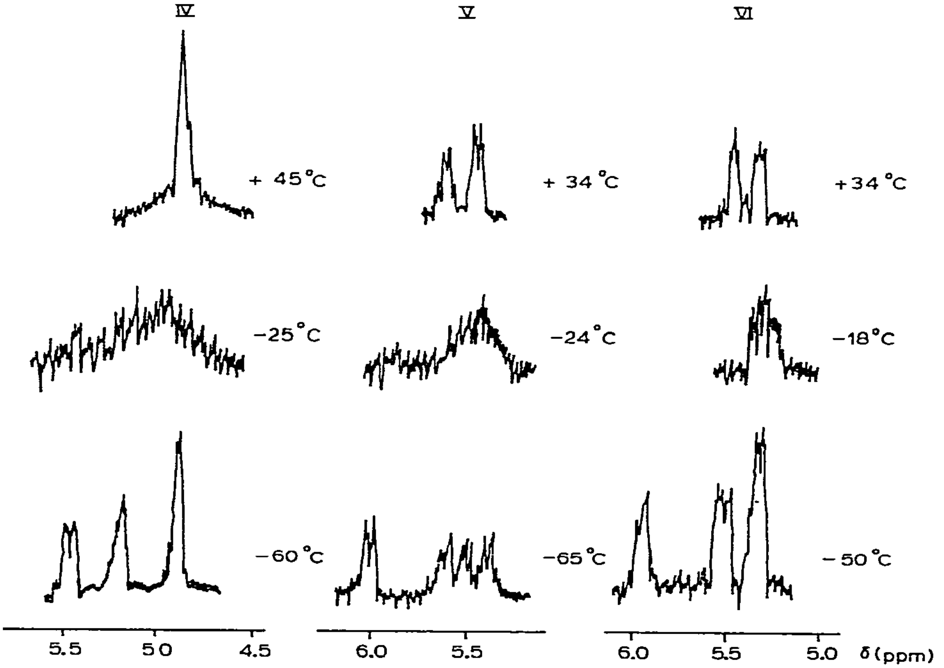


Fig. 1. Temperature dependence of the ^1H NMR spectra of the cyclopentadienyl rings of $[C_5H_4CHN(CH_3)_2]M(CO)_3$ in acetone. IV, M = Cr; V, M = Mo; VI, M = W.

TABLE 2

ENERGY PARAMETERS FOR THE BARRIERS TO ROTATION ABOUT THE C(6)—N BOND AND CHEMICAL SHIFTS OF THE CARBON ATOM C(6) OF 6-DIMETHYLAMINOFULVENE (III) AND ITS COMPLEXES WITH CARBONYLS OF CHROMIUM (IV) MOLYBDENUM (V), AND TUNGSTEN (VI)

Compound	Solvent [a]	E_{act} (kcal mol^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (entr. un.)	$\Delta G^{\ddagger}_{298}$ (kcal mol^{-1})	τ (s) (34°C)	δ (C(6)) [d] (ppm)
III	Acetone	13.9 ± 0.2	13.3 ± 0.2	−2.5 ± 1.0	14.0 ± 0.2	0.0194 [e]	148.8
IV	Acetone	—	—	—	17.9 ± 0.2 [c]	1.1	154.9
V	Acetone	25.3 ± 0.7	24.7 ± 0.7	25.0 ± 2.0	17.3 ± 0.4	0.162	153.1
	Nitromethane	22.0 ± 0.6	21.3 ± 0.6	12.0 ± 1.0	17.7 ± 0.4	0.48	
	DMF [a]	21.2 ± 0.6	20.5 ± 0.6	7.4 ± 1.0	18.3 ± 0.4	1.1	
VI	Acetone	24.9 ± 1.0	24.3 ± 1.0	27.3 ± 2.0	16.2 ± 0.5	0.0334	150.13

[a] Dipole moments (μ, D) of solvents: acetone 2.7, nitromethane 3.1; DMF 3.8 [5]. [b] DMF = dimethylformamide. [c] The calculation is based on the rate data at a temperature of +52°C at which only broadening of the methyl group signals is observed. [d] In acetone at +25°C. [e] At 8°C.

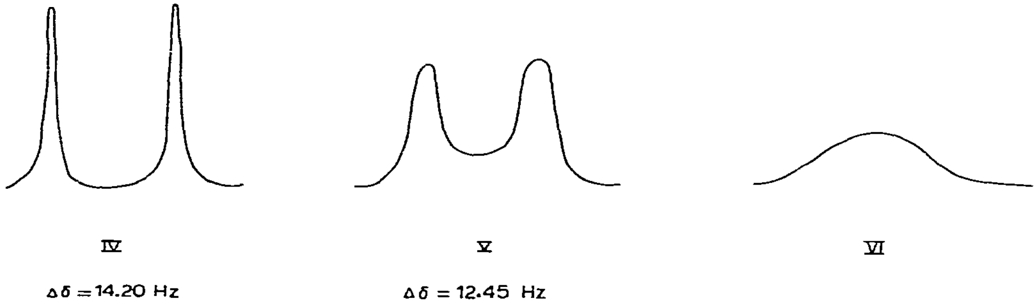


Fig. 2. ^{1}H NMR spectrum of the methyl groups of $[C_5H_4CHN(CH_3)_2]M(CO)_3$ in acetone at 34°C (5 Hz per cm); IV, M = Cr; V, M = Mo; VI, M = W.

C(6)—N bond of compounds III—VI, summarized in Table 2, were determined from a complete analysis of the shapes of the lines [3] of the proton signals of the methyl groups bonded to the nitrogen atom.

The low-temperature (—50 to —65°C) NMR spectra of the chromium (IV) and tungsten (VI) complexes in acetone show three separate signals for the hydrogen atoms in the five-membered ring, having a fine structure, while the spectrum of the molybdenum (V) complex contains four signals (Table 1, Fig. 1). At higher temperature these signals are broadened and coalesce to a wide signal which is then, as the temperature rises further, transformed either to one (M = Cr) or two (M = Mo, W) single singlets (Fig. 1), depending on the nature of central metal atom of the complexes. The temperature-induced changes in NMR spectra of the cyclopentadienyl rings can be explained by the molecule overcoming the barriers to rotation about the C(1)—C(6) bond of compounds IV—VI. Comparison of the results with the temperature-dependence of the ^{1}H NMR spectra of the parent 6-dimethylaminofulvene (III) [4] indicates that the coalescence of the proton signals in the cyclopentadienyl rings of complexes IV—VI is observed at a temperature ($\leqslant$—18°C) much lower than in the case of the original fulvene (+148°C, dimethylsulfoxide [4]). This suggests that the coordination of fulvene III with Group VIB metal carbonyls (Cr, Mo, W) lowers the barrier to the rotation about the C(1)—C(6) bond, and hence, decreases the degree of double-bond character between the C(1) and C(6) atoms.

The temperature-dependence of the ^{1}H NMR spectra of the protons of the methyl groups bonded to the nitrogen atom in compounds III—VI was used to evaluate the variation in the degree of double-bond character between the C(6) and N atoms in the parent fulvene III during coordination with the transition metal carbonyls. It was found, for example, that at a low temperature, the spectra of the complexes IV—VI in acetone show two separate proton signals for the $—N(CH_3)_2$ groups, which coalesce to a single singlet at higher temperatures. The temperature at which the signals of these protons in IV—VI coalesce depends on the nature of the central metal atom, and increases in the sequence VI < V < IV (W < Mo < Cr) and equals +34, +48, and >+52°C, respectively. As far as the parent fulvene III is concerned, the methyl group signals coalesce at a temperature below +8°C. The free energy for the rotational barriers for rotation about the C(6)—N bond of complexes IV—VI equals 17.9, 17.3, and 16.2 kcal mol^{-1} (25°C, acetone), respectively, and that of non-coordinated fulvene

III is 14.0 kcal mol^{-1} (Table 2). Hence, the free energy for the barrier to rotation about the C(6)—N bond of the original fulvene increases after its coordination with carbonyls of W, Mo, and Cr by 2.2, 3.3, and 3.9 kcal mol^{-1}, respectively, which is indicative of a greater degree of double-bond character between the C(6) and N atoms in the sequence III < VI < V < IV.

Thus, the π-coordination of fulvene III with Group VIB metal carbonyls is accompanied by a decrease in the degree of double-bond character between the C(1) and C(6) atoms with a simultaneous increase in the C(6)—N bond order, that is by an increase in ligand polarity; the change in the degree of double-bond character being strongly dependent on the nature of the central metal atom, increasing in the sequence W < Mo < Cr.

This conclusion agrees with the results of X-ray analysis [6,7] and ^{13}C NMR spectroscopy [8] of 6-dimethylaminofulvene (III) and its tricarbonylchromium complex (IV), according to which, as a result of the π-coordination of III with the carbonyl of chromium, the lengths of the C—C bonds in the cyclopentadienyl ring are averaged, the length of the C(1)—C(6) bond increases, that of the C(6)—N bond decreases, the electron density at the carbons of the cyclopentadienyl ring is averaged, and their screening becomes more pronounced, i.e. the polarity of the fulvene ligand increases.

The greater polarity of fulvene III as a consequence of its coordination with the transition metal atom must cause an increase in the positive charge at the exocyclic carbon, C(6), as well as a downfield shift of the signals from the C(6) nuclei in the ^{13}C NMR spectrum. Indeed, it was found that there is direct proportionality between the free energy for the barriers to rotation about the C(6)—N bond and the chemical shifts of the C(6) atoms of complexes IV—VI (Table 2, Fig. 3) *.

It is well known that the magnitude of the rotational barrier may be strongly influenced by the nature of the solvent medium. This is why we studied the rotational isomerism of 6-dimethylaminofulventricarbonylmolybdenum (V) in solvents of varying polarity, namely acetone, nitromethane, and DMF. As a result, the effect of the solvent on the magnitude of the rotational barrier for rotation about the C(6)—N bond was found to increase in the sequence acetone < nitromethane < DMF, $\Delta G^{\ddagger}$ being equal to 17.3, 17.7 and 18.3 kcal mol^{-1}, respectively. The effect of the solvent becomes so significant that the rotational barrier in the molybdenum complex V becomes greater in dimethylformamide than that in the chromium complex IV in acetone.

$\Delta G^{\ddagger}$ and the dipole moment of the solvent are directly proportional (Table 2, Fig. 4): the greater the dipole moment, the higher the free energy for the barrier to rotation about the C(6)—N bond. Hence, the interaction between the complex molecules and the polar aprotonic electron-donor solvents examined is determined, primarily, by the electrostatic forces and is essentially a dipole—dipole interaction.

Thus, as a result of our studies into the rotational isomerism of complexes IV—VI in solvents of differing polarity by dynamic ^{1}H NMR spectroscopy, we determined the energy parameters of the barriers restricting rotation about the C(6)—N bond and demonstrated that (a) the coordination of 6-dimethylamino-

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* The ^{13}C NMR spectra of complexes IV—VI will be covered at greater length in a subsequent paper.

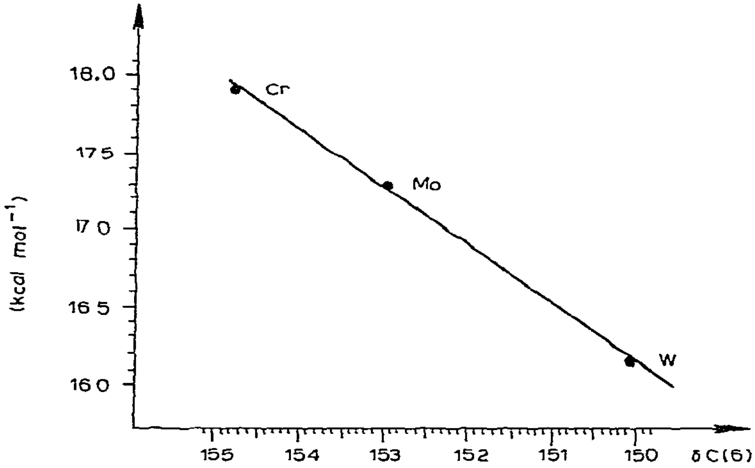

Fig. 3. Free energy $\Delta G^{\ddagger}$ for the barrier to rotation about the C(6)—N bond of $[C_6H_4CHN(CH_3)_2]M(CO)_3$ versus chemical shift of the carbon C(6); M = Cr, Mo, W.

fulvene (III) with Group VIB transition metal carbonyls increases the free energy for the above barrier, i.e. increases the degree of double-bond character between the C(6) and N atoms; (b) the free energy for the rotational barriers (hence, the ligand polarity) are strongly dependent on the nature of the central metal atom, increasing in the sequence W < Mo < Cr; (c) the positive charge at the exocyclic carbon C(6) increases with increasing polarity of the π-ligand, due to the greater degree of double-bond character between the C(6) and N atoms; and (d) the increasing polarity of the solvent in the sequence acetone < nitromethane < DMF raises the rotational barrier as a result of the dipole—dipole interaction between the complex and solvent molecules.

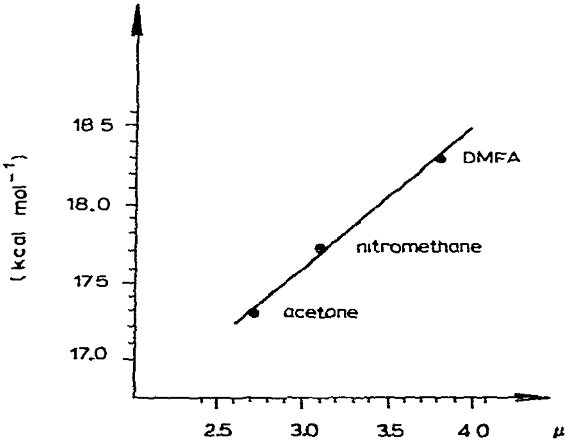

Fig. 4. Free energy $\Delta G^{\ddagger}$ for the barrier to rotation about the C(6)—N bond of $[C_5H_4CHN(CH_3)_2]$-$Mo(CO)_3$ versus dipole moment μ of the solvent.

Experimental

Complexes IV—VI were obtained by the method described in ref. 9.

We used completely deuterated solvents, which were purified and dried in argon atmosphere. The solutions were prepared and ampoules filled also under argon.

The ^1H NMR spectra were recorded on an RYa 2309 spectrometer at 90 MHz The temperature was maintained accurately to ±1°C.

The lifetimes τ of the rotamers of complexes IV—VI and initial fulvene III were estimated by comparing the experimental spectra of the —$N(CH_3)_2$ indicator groups with the calculated values. The difference in the chemical shifts $\Delta\delta CH_3$, used for calculating the spectra, was found by extrapolating the observed temperature dependences of the given parameters in the absence of transitions to the region of rapid exchange [3]. The spectra of the —$N(CH_3)_2$ groups were computed on a PDP 12 computer using a routine written in Arnold's formalism [10].

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