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Barriers to rotation about the C(O)–N bond in tricarbonylchromium complexes of aromatic *N,N*-dialkylamides

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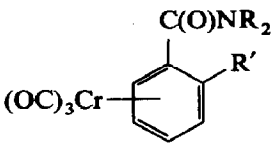
Abstract

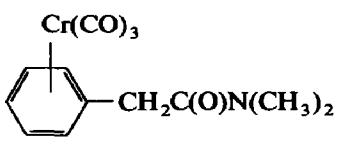
The variable-temperature ^{1}H NMR spectra of tricarbonylchromium complexes of five aromatic *N,N*-dialkylamides have been recorded to determine the barrier to amide rotation. Low-temperature ^{13}C NMR spectra have also been recorded in some cases to support conclusions concerning the stereochemistry of the investigated compounds. Complexation of the arene ring causes a considerable modification of the stereodynamics of the amide molecule. The origin of the observed effects is discussed.

Introduction

This paper presents the recent results of our NMR studies on the influence of various structural factors on the internal rotation about the amide C(O)–N bond in *N,N*-dialkylbenzamides [1-4]. It concerns the effect of complexation of arene ring by tricarbonylchromium group on the height of the barrier to amide rotation. The stereodynamics of the amides modified in this manner have not yet been studied. As model compounds we have prepared tricarbonylchromium complexes of following amides: *N,N*-dimethylbenzamide (1), *N,N*-diethylbenzamide (2), *N,N*,2-trimethyl-



	R	R′
1	CH_3	H
2	C_2H_5	H
3	CH_3	CH_3
4	C_2H_5	CH_3



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benzamide (**3**), *N,N*-diethyl-2-methylbenzamide (**4**), and *N,N*-dimethylphenylacetamide (**5**). All but one of them (**1**, [5]) are novel.

Results and discussion

Interpretation of the static ^1H and ^{13}C NMR spectra

At sufficiently low temperatures the internal rotation about amide C(O)–N bond is restricted in all the complexes investigated, and their ^1H NMR spectra show separate signals of (*E*)- and (*Z*)-*N*-alkyl groups: two singlets for *N*-methyl protons of compounds **1**, **3**, and **5**, two A_3B_2 triplet-quartet patterns for *N*-ethyl groups in **2** and two, partially overlapped in the BC part, A_3BC multiplets for *N*-ethyl groups of **4**. Whereas the spectra of the *N*-alkyls for **1**–**3** and **5** are fully comprehensible, the interpretation of spectrum of **4** requires a short comment. Spectra similar to that of **4** were observed at low temperatures for uncomplexed 2-substituted *N,N*-diethylbenzamides. These spectra were assumed to provide evidence for a restricted rotation about aryl–C(O) bond [6,7]. 2-Substituted *N,N*-diethylbenzamide derivatives exist in solution as a mixture of enantiomeric conformers because of twisting by the aryl and amide planes. In such conformers the geminal methylene protons are diastereotopic and can be anisochronous when the aryl-C(O) rotation is restricted. The stereochemistry of complex **4** is, however, different. Because its molecule is chiral, the geminal methylene protons might be anisochronous even if all the internal rotations about the formal single bonds are fast. In conditions of restricted rotation about aryl–C(O) bond rotamers are diastereomeric and could give separate spectra. Even at the lowest temperatures, close to freezing point of the solvent used (acetone-d_6, m.p. $-94\,^\circ C$), we observed only the one sharp singlet from the 2-methyl group and only the one pair of triplets from the methyls of the *N*-ethyl groups. If one excludes the accidental degeneracy of the spectra of the rotamers mentioned, the above observation may be explained on the assumption that there is either rapid rotation about the arene–C(O) bond or predominance (> 95%) by one of the conformers. Keeping in mind the fact that it is possible to freeze out arene–C(O) rotation in the free ligand [7] the former hypothesis seems to be less probable. Considering all the electronic and steric interactions and taking into account X-ray data for some analogous compounds [8,9] we think that in the energetically favourable conformation the aromatic ring and the amide moiety are not coplanar and the carbonyl oxygen is located on the side of the ring plane opposite the chromium tripod, close to the 2-methyl group (Figure 1). In conditions of restricted aryl–C(O)N rotation similar effects in the spectra of **1** and **2** may also be expected. For both compounds the carbons of the aromatic ring should give six rather than four signals, and the geminal methylene protons of **2** could be anisochronous. None of these effects were, however, observed at temperatures above $-88\,^\circ C$. Full rotation about the arene–C(O)N bond is, however, not necessary for averaging the magnetic environments of the aromatic carbons in **1** and **2** and geminal methylene protons in **2**. Thus we can only conclude that the passage through a state in which the phenyl ring and the amide plane are perpendicular to each other has a very low activation energy.

Rotation about C(O)–N bond

When the temperature of measurement is increased characteristic, dynamic

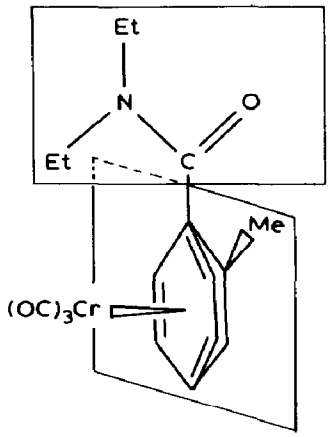

Fig. 1. The most probable conformation of (η^6-N,N-diethyl-2-methylbenzamide)tricarbonylchromium complex.

changes in the *N*-alkyl group regions of the ^{1}H NMR spectra are observed. These changes are caused by the increasing rate of rotation about C(O)–N bond. At 60 °C averaging is almost complete for the compounds **1**, **2** and **5** whereas the signals from **3** and **4** are still strongly broadened. The total line shape analysis of the averaging methyl singlets (**1**, **2** and **5**) or triplets (**2** and **4**) was performed by the standard non-linear least-squares method optimizing at least five of the following line shape parameters: exchange rate, mean chemical shift, total intensity, base line level, contributions by the dispersion mode spectrum, static difference of the chemical shifts, and coupling constants. The presence of the free ligand signal in the spectrum of **5** was also taken into account during the calculations. In the case of averaging ethyl groups we have found that optimising the mean value of both vicinal coupling constants and the difference between them is more convenient than optimising coupling constants themselves. In all cases the difference between vicinal coupling

Table 1

^{1}H NMR chemical shifts [a] and melting points of investigated complexes.

Compound	Melting point (°C)	N—CH_3 or N—CH_2CH_3	N—CH_2CH_3	Ar—CH_3	Aromatic protons
1	97– 99 [b]	3.015			5.85 (H-2, H-6); 5.60 (H-4); 5.48 (H-3, H-5)
2	121–123	1.134	3.408		5.78 (H-2, H-6); 5.57 (H-4); 5.47 (H-3, H-5)
3	128–131	2.978		2.160	5.74 (H-6); 5.61 (H-4);
		2.889			~ 5.3 (H-3, H-5)
4	115–118	1.149	3.59; 3.28 [c]	2.157	5.77 (H-6); 5.59 (H-4);
		1.044	3.22; 3.26		5.29 (H-3); 5.26 (H-5)
5	[d]	2.58		3.41 [e]	~ 5.4

[a] δ(ppm) in acetonitrile-d_3 solution. [b] Lit [5] 96–98 °C. [c] Determined from decoupling experiments. [d] Unstable, usually contaminated with ligand. [e] ArCH_2C(O)NMe_2.

Table 2

^{13}C NMR chemical shifts (δ ppm) of some of investigated complexes

Complex	$Cr(CO)_3$	C(O)N	$N-CH_3$ or $N-CH_2CH_3$	$N-CH_2CH_3$	$Ar-CH_3$	Aromatic carbons	Solvent
2	233.7	165.8	14.4 12.7	43.7 40.5		109.4 (C-1); 95.8 (C-2); 95.5 (C-2, C-6); 91.6 (C-3, C-5)	$(CD_3)CO$
3	234.3	166.5	36.0 38.0		18.7	113.6 (C-1); 110.5 (C-2); 97.1 (C-4); 96.0 (C-6); 92.2 (C-3); 88.8 (C-5)	CD_3CN
4	232.1	164.4	14.0 12.6	42.9 39.7	18.2	111.3 (C-1); 106.7 (C-2); 93.8 (C-4); 92.4 (C-6); 89.7 (C-3); 86.2 (C-5)	CD_3CN

constants did not exceed 0.1 Hz. This permitted us to assume a zero value for that parameter and to optimise it, if at all, in the final steps of iteration process. In the case of complex **4** we have dealt with the exchange of spin systems A_3BC and D_3EF for which formally four different vicinal coupling constants should be taken into consideration. In the low temperature spectra the methyl groups of **4** gave two sharp triplets, so during the analyses we could assume that $J_{AB} = J_{AC}$ and $J_{DE} = J_{DF}$. For each compound at temperatures in which the rotation rate was determined with an accuracy of better than 30% the free energy of activation, $\Delta G^{\neq}$, was calculated by use of the Eyring equation. Averaged values of $\Delta G^{\neq}$ calculated for the various temperatures are collected in Table 3. A procedure to estimate the barrier heights is based on the common assumption that the entropy of activation of amide rotation is small [10]. Data presented in Table 3 show that the barriers to the amide rotation in the complexes **1**–**4** are lower than those in the free ligands. Moreover, the effect of complexation decreases with increased steric crowding around the axis of rotation.

In an attempt to rationalize our results, two types of interactions between

Table 3

Barriers to amide rotation in tricarbonylchromium complexes of *N,N*-dialkylamides

No.	Ligand	$\Delta G^{\neq}_{ligand}$	$\Delta G^{\neq}_{compl}$	$\Delta G^{\neq}_1 - \Delta G^{\neq}_c$
1	$C_6H_5CON(Me)_2$	69.1	57.8	11.3
2	$C_6H_5CON(Et)_2$	62.9	55.8	7.1
3	*o*-$MeC_6H_4CON(Me)_2$	73.5	67.0	6.5
4	*o*-$MeC_6H_4CON(Et)_2$	72.3	69.0	3.3
5	$C_6H_5CH_2CON(Me)_2$	74.5	74.4	0.1
6	*p*-$NO_2C_6H_4CON(Me)_2$	75.2		

tricarbonylchromium and amide moieties were taken into account: a direct, through space interaction involving steric and other electrostatic repulsion and through electron interaction involving effects arising from the change in electronic structure of the complexed ligand. Interaction of the first type probably forces the amide group into a position coplanar with the aromatic ring. Such a change in conformation would destabilize sterically the ground state of amide rotation. At the same time the $\pi-\pi$ conjugation of the carbonyl and aromatic electrons, which is more effective in the transition state of the rotation, would be intensified. The total influence of direct interaction is to some extent analogous to that of the hydrogen bond in salicylamides [1,11] and should decrease the activation barrier to amide rotation. It is not clear, however, why such a mechanism of interaction is less in evidence for compounds **3** and **4** than for **1** and **2**.

It is difficult to predict which direction the influence of the second type of interaction has on the barrier to amide rotation. The abundant data in the literature concerning the properties of arenetricarbonylchromium complexes may lead to contradictory conclusions. Solladié-Cavallo, in a review [12], has presented several experimental facts which confirm that the complexation of the aromatic ring increases its electron withdrawing properties (inductive effect) and stabilizes the negative charge at the carbon atom bonded to the ring. It has been found that complexation of the ring has the same effect as its substitution by a nitro group [13]. It seems from our results that the effects of $C_6H_5-Cr(CO)_3$ and $C_6H_4NO_2$ are similar to each other when the group experiencing that influence is separated from the ring. Complexation of the aromatic ring of *N,N*-dimethylphenylacetamide (**5**) or its substitution by NO_2 group (**6**) results in similarly small changes in the barrier to rotation. On the other hand it is well documented that the increase of the inductive effect by X in $XC(O)NR_2$ increases the barrier to amide rotation [10,14]. Even more effective is a nitro substitution in the aromatic ring of benzamide; $\Delta G^{\neq}$ values for *N,N*-diethylbenzamide and its 4-nitro derivative are 65.2 and 68.5 kJ/mole, respectively [2,10]. Our results, however, indicate that complexation lowers the barrier to amide rotation which is in obvious contradiction to the above expectation. Numerous experimental examples in which complexation acts in the opposite direction are described in a review [12]. For many arene complexes it has been found that the tricarbonylchromium group stabilizes the positive charge at the α position. That stabilization is attributable to the direct interaction of the filled chromium *d*-orbitals with the positive charge center. The increased polarizability of the complexed ring could also be involved. Especially relevant are the data documenting the increased basicity of oxygen in complexed arene derivatives of the type: ArC(O)X (X = H, alkyl) [5]. Such an interaction between tricarbonylchromium group and amide carbonyl carbon obviously lowers the barrier to amide rotation, a feature that is in accord with our observations. It also explains, why in the case of complexes **3** and **4**, the amide rotation is less influenced by complexation than in the case of compounds **1** and **2**. Namely, the interaction between the $Cr(CO)_3$ and the amide moieties in the compounds **1** and **2** is weaker owing to the larger twist of the amide group out of the arene plane. It is noteworthy, that the rationalization of our results taking into account the electronic effects of $Cr(CO)_3$ moiety is one of hindsight.

Experimental

The tricarbonylchromium complexes were synthesized by use of a standard method [15]. Elemental analysis data for complexes **1–4** are in accord with the assigned structures. We did not succeed in obtaining a pure sample of complex **5**. It was unstable and usually contaminated with ligand. Melting points and ^{1}H, and ^{13}C NMR data are listed in Tables 1 and 2, respectively. Solutions of the complexes in acetonitrile-d_3 were prepared and filtered through SiO_2 directly into the NMR tubes under argon. The tubes were sealed under vacuum and stored at 4 °C. The ^{1}H NMR spectra of **1**, **3**, **5** and *p*-nitrophenyl-*N*,*N*-dimethylacetamide were recorded on by a Tesla BS 567A spectrometer operating at 2.3 T. The ^{1}H NMR spectra of **2** and **4** and the ^{13}C NMR spectra of all the compounds investigated were measured using Bruker AM-500 spectrometer operating at 11.7 T. The temperature was calibrated with methanol or ethylene glycol standards. The dynamic spectra were digitized by hand. Their shapes, usually represented by 100–200 points, were analysed using a modified version of the NMRAB program written in PROFORT with the aid of an IBM PC XT microcomputer. The algorithm used is based on a gradient, non-linear, least-squares method for iterative fitting of experimental and theoretical data. The line shape of the exchanging spin systems was described by the function originated from the GMS theory [16].

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