

The first isolation of a π -complex precursor in Meisenheimer complex formation

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Treatment of 1,3,5-trinitrobenzene with indole-3-carboxylate ion in methanol affords an isolable π -complex which is the precursor of the N- and C-adducts expected from the interaction.

While the intermediacy of anionic σ -complexes in nucleophilic aromatic substitution is now well established,^{1–5} the role of charge-transfer (CT) or π -complexes in such processes remains controversial.^{6–10} A variety of experimental methods have provided evidence for the formation of CT or π -complexes in the interaction of electron-deficient aromatics (acceptors) and bases/nucleophiles (donors), but it is uncertain whether these species are formed in competing processes, concurrently, or whether they are present as intermediates on the S_NAr reaction pathways. In a series of papers by Bunton and co-workers evidence has shown that π -complexes and charge-transfer (electron-transfer) complexes are formed prior to the anionic covalent σ -complex adducts, enroute to S_NAr displacement, and are also intermediates in H/D exchange.^{11–15} However, to our knowledge there has been no report so far of the actual isolation of CT or π -complexes in S_NAr or σ -complex formation processes with a simple (classical) nitroaromatic compound such as 1,3,5-trinitrobenzene.¹⁶ In this report we present evidence for the first instance of this kind.

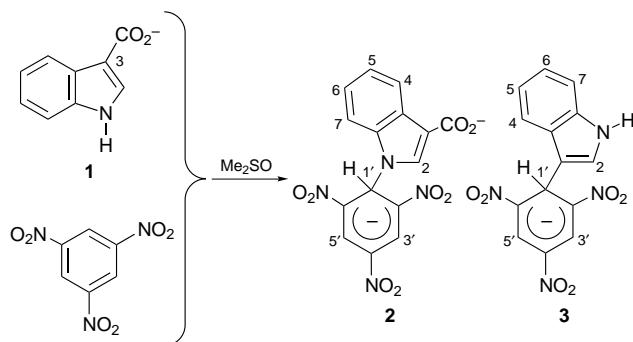
The reaction of 1,3,5-trinitrobenzene (TNB) with indole-3-carboxylate (**1** as Na⁺ salt) in Me₂SO, as followed by NMR

spectroscopy, gives rise to the TNB N-adduct **2** concurrently with the TNB C-adduct **3** formed through decarboxylation (Scheme 1). These adducts could readily be characterized by ¹H and ¹³C NMR spectroscopy (Table 1).^{2,3}

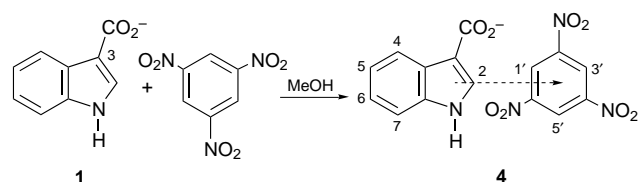
However, when carried out in methanol the reaction takes a different course. This reaction gives rise to an adduct which can be isolated from the solution as the sodium salt and which we formulate as the π -complex **4** (Scheme 2). The adduct can be simply prepared by mixing 0.2 M methanolic solutions of TNB and indole 3-carboxylate (Na⁺ salt) and evaporating to dryness.

This brown solid has been characterized as follows. The UV–VIS spectrum contains new bands (not present in TNB or **1**) of low intensity characteristic of π - or CT complexes¹⁷ at 385, 413, 474 and 500 nm. Especially noteworthy in the ¹H NMR spectrum (Table 1) is the substantial shift to high field of the protons relative to the parent nitro-aromatic ($\Delta\delta = 0.50$ ppm).¹⁸ ESI mass spectroscopy experiments show the expected peak corresponding to the molecular ion of **4** (*m/z* 373). Also, CAD (collision activated dissociation) of this molecular ion shows the required daughter peaks, *i.e.* the indolecarboxylate (*m/z* 160) and TNB, actually (TNB – H)[–], (*m/z* 212) portions.

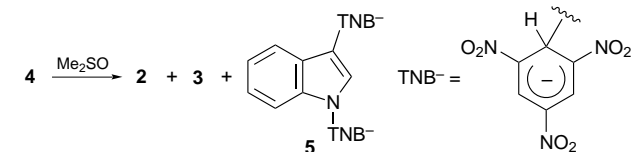
Interestingly, when **4** is placed in Me₂SO, it rapidly gives rise to the TNB N-adduct **2**, the TNB C-adduct **3** formed upon



Scheme 1



Scheme 2



Scheme 3

Table 1 NMR parameters for the π -complex **4** and the σ -adducts **2** and **3**^{a,b}

Compound	H _{1'}	H _{3',5'}	H ₂	H ₄	H ₅	H ₆	H ₇	NH	Coupling constants/Hz
2 ^c	7.36	8.59	7.56	8.09	7.10	7.15	7.33	—	H ₄ –H ₅ = 8.07; H ₆ H ₇ = 8.46; H ₅ –H ₇ = 1.11
3 ^c	5.98	8.36	7.16	7.49	6.95	7.03	7.30	11.01	H ₄ –H ₅ = 7.71; H ₄ –H ₆ = 1.47; H ₆ –H ₇ = 7.71; H ₅ –H ₇ = 1.11; H ₂ –NH = 2.22
4 ^d	8.83	8.83	7.68	8.02	6.95	6.95	7.20	^e	—

^a For comparison: TNB (CD₃OD) δ : 9.33; TNB [(CD₃)₂SO] δ : 9.19. ^b ¹³C NMR of **4** (0.45 M) in CD₃OD: CO, δ : 174.83; C_{2/6/4'}, 149.09; C_{3/5/1'}, 123.99; C₂, 130.69; C₃, 115.47; C₄, 122.37; C₅, 120.96; C₆, 122.45; C₇, 112.18; C₈, 137.73; C₉, 128.00. ^c Solvent: (CD₃)₂SO; internal reference Me₄Si. ^d Solvent: CD₃OD; internal reference Me₄Si. ^e Exchangeable proton in CD₃OD.

decarboxylation, and the N–C diadduct **5** (Scheme 3). The mono-adduct **3** and the diadduct **5** were obtained previously from the direct reaction of TNB with indolide ion under more basic experimental conditions.¹⁹

While indole itself has been known to form a molecular complex with TNB,²⁰ the use in the present work of the indole-3-carboxylate ion (**1**) has allowed solubilization in methanol and, equally importantly, has increased charge density of the indole nucleus, thus stabilizing the π -complex.

Further work towards definitive characterization of π -complexes in these systems will be concerned with X-ray structure determination, kinetic studies, and structural variation of the indole moiety with the view of modulating the stability of these complexes.

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Footnotes

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