(10) The foreruns from the work-up of NMDPP and MDPP syntheses were redistilled to recover diphenylphosphine. The fraction boiling at 99–100° (1.0 mm) was collected.

(11) Precautions should be taken during all stages of the work-up of NMDPP and MDPP to limit contact with air as much as possible, and thus reduce the amount of oxide formed as a by-product.

(12) Melting points of NMDPP and MDPP samples vary slightly from preparation to preparation depending on the amount of oxide present.

(13) Methenes and diphenylphosphine are by-products in the sodium diphenylphosphide reactions. These products apparently result from elimination reactions in which the phosphide anion functions as a base rather than as a nucleophile. The elimination side reactions are the primary reason for the relatively low yields of the desired tertiary phosphines. Elimination is, as expected, a more serious competitive process in the case of neomenthyl chloride. The diphenylphosphine, which results from the elimination reaction and hydrolysis of unreacted sodium diphenylphosphide, can be recovered.[10]

(14) There is a recent literature report,[4b] without experimental details, that gives $[\alpha]^{20}\text{D}$ −95.7° (c, 1.07, $CH_2Cl_2$).

# The 1,3,5-Trinitrobenzene–*N*-Methylanilide $\sigma$ Complex

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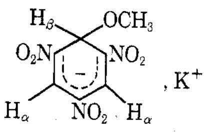
While $\sigma$ complex formation between polynitroaromatic compounds and aliphatic amines has been well established,[1,2] only one instance of a $\sigma$ complex involving an aromatic amine has been reported.[3] In the previous communication[3] we presented spectral evidence (nmr and uv-visible) which strongly suggested that the product of the reaction between the methoxide ion–1,3,5-trinitrobenzene (TNB) $\sigma$ complex **1** and aniline in dimethyl sulfoxide (DMSO) solution was the anilide $\sigma$ complex **2**.

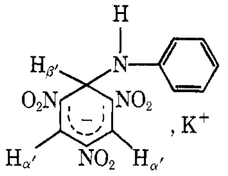
In an effort to confirm our earlier conclusions, we have extended the study to include the reaction of **1** with *N*-methylaniline. It was envisaged that use of this amine would result in an unambiguously interpretable nmr spectrum, since the NH-$H_{\beta'}$ coupling which was evident in **2** will have been removed in the anticipated $\sigma$ complex **3**. Our previous findings of a relatively sharp AB quartet with a large coupling constant for the $\sigma$ complex **2** was unexpected, as the observation of sharp doublets for NH protons coupled to CH is a relatively rare occurrence.[4,5] In view of the fact that we are concerned with structural identification of a novel complex, it was desirable to have at least one case where this feature would be absent from the nmr spectrum. In practice it turned out that the choice of *N*-methylaniline was only partially successful, as a result of interference from the aromatic protons of the amine; however, use of *N*-methylaniline-*2,4,6*-$d_3$ led to the desired simplification in the nmr spectrum and has thus allowed complete structural identification of the aryl amine $\sigma$ complex.

After **1** was mixed with *N*-methylaniline in DMSO solution the following nmr spectral changes were observed. A spectrum taken 45 min after mixing exhibited the $H_\alpha$, $H_\beta$, and $OCH_3$ absorptions typical for **1** at 8.48 (doublet, $J$ = 1.2 Hz), 6.16 (unresolved triplet), and 3.20 ppm (singlet), respectively; and for *N*-methylaniline typical multiplets in the aromatic proton region due to the ring protons, a broad singlet at 5.4 ppm for the amino proton, and a doublet ($J$ = 5 Hz) centered at 2.63 ppm attributed to the *N*-methyl group. In addition there were present a small signal 0.05 ppm downfield from $H_\alpha$ and assigned to $H_{\alpha'}$ of **3**, and a singlet at 2.30 ppm which corresponds to the methyl protons in the *N*-methylaniline moiety of **3**. With time further development was evident for the peaks attributed to **3** and those due to methanol (quartet, $J$ = 5 Hz at 4.0 ppm; doublet, $J$ = 5 Hz at 3.1 ppm), while those belonging to **1** and *N*-methylaniline steadily decreased. The changes were observed to be complete within 1 day.

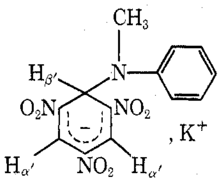
The signal expected for $H_{\beta'}$ in **3** was not observed, implying that it is "buried," likely under the aromatic proton multiplets which are centered at *ca.* 6.8 ppm. In order to locate the position of the $H_{\beta'}$ absorption, *N*-methylaniline-*2,4,6*-$d_3$ was treated with **1**. In DMSO solutions the 3 and 5 protons in the *N*-methylaniline-*2,4,6*-$d_3$ give rise to a single peak at 7.03 ppm. On reaction of this amine with **1**, two new features are discernible from the nmr spectra. Firstly, a peak at 7.13 ppm increases at the expense of the signal at 7.03 ppm and is assignable to the ring protons in the partially deuterated *N*-methylaniline moiety of the complex **3**. Secondly, the growth in a peak at 6.63 ppm corresponds to the decrease in intensity of the $H_\beta$ signal and is assigned to $H_{\beta'}$. Thus the nmr parameters for the $\sigma$ complex can be assigned: $H_{\alpha'}$ 8.53 ppm, $H_{\beta'}$ 6.63 ppm, $NCH_3$ 2.30 ppm.



**1**



**2**



**3**

The reaction between *N*-methylaniline and **1** in DMSO was also followed by means of visible spectroscopy. Using solutions of comparable concentrations to those used in the nmr experiments, visible spectra were recorded periodically, following a 100-fold dilution with DMSO. The reaction was observed to be accompanied by a decrease in the 427- and 509-nm absorptions due to **1** and the development of absorption maxima at 436 and 516 nm due to product formation. Interconversion of the two absorbing species was characterized by reasonably tight isosbestic points. The double absorptions with the higher energy maximum being more intense are of course typical of $\sigma$ complexes of TNB.[6-9]

The nmr and visible absorption spectral data presented above are fully consistent with the formation of the $\sigma$ complex **3**. It may be concluded that the reaction of the TNB–methoxide ion complex **1** with primary or secondary aromatic amines in DMSO solution, leading to formation of TNB–aryl amine $\sigma$ complexes, appears to be a general type of reaction.

Further examination of the nmr parameters for the complex **3** reveals additional information with probable structural significance. It will be noted that the nmr peaks of protons in the aromatic amine are shifted to low field on complex formation. This may be ascribed to the electron-withdrawing ability of the 2,4,6-trinitrocyclohexadienate moiety relative to an amino proton. Contrasting to the low-field shift of the aromatic protons of the amine moiety is the observed shift to high field of the *N*-methyl proton resonance on formation of **3**. This observation suggests that the methyl group protons experience an anisotropic effect due to preferential orientation above the 2,4,6-trinitrocyclohexadienate ring. It would appear that nmr should be of value in providing structural elucidation of aromatic amine–TNB $\sigma$ complexes.

## Experimental Section

**Materials.** 1,3,5-Trinitrobenzene was recrystallized from ethanol and dried *in vacuo,* mp 123–123.5°. DMSO (Fisher Certified Reagent) was distilled from barium oxide under nitrogen at reduced pressure and the middle fraction boiling at 44° was collected and stored in the dark.[2] *N*-Methylaniline was distilled from zinc dust under reduced pressure.

***N*-Methylaniline-*2,4,6-d*$_3$.** *N*-Methylaniline (6 ml) was added to a solution of $D_2O$ (30 ml), ethanol-*O-d* (10 ml), and concentrated $D_2SO_4$ (6 ml) and the mixture was heated under reflux overnight. The reaction solution was then neutralized with saturated bicarbonate and extracted with ether; the extracts were dried and the ether was removed. Distillation *in vacuo* yielded *N*-methylaniline-*2,4,6-d*$_3$, which was shown by nmr to contain *ca.* 6% of the undeuterated material.

**Potassium 1-Methoxy-2,4,6-trinitrohexadienate (1).** The $\sigma$ complex **1** was prepared from methanolic potassium methoxide and TNB, under nitrogen, followed by precipitation with dry benzene.[10] Filtration, washing with dry ether, and drying *in vacuo* yielded **1** as an orange-red solid.

**Spectral Characterization of $\sigma$ Complex 3.** The nmr spectra were obtained with a Varian 60-MHz instrument at 35° on the DMSO-$d_6$ reaction solutions containing the $\sigma$ complex 1 (0.40 *M*) and the aromatic amine (0.44 *M*). The spectrum was scanned periodically from the time of mixing. Tetramethylsilane was used as an external standard.

The visible spectra were obtained on a Unicam SP800 spectrophotometer following a 100-fold dilution with DMSO. The spectra were taken in a 0.1-mm cell.

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