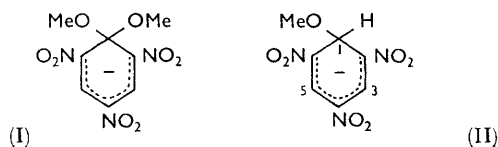


**824. Reactions of Aromatic Nitro-compounds in Alkaline Media. Part IX.\* Nuclear Magnetic Resonance Spectra of Meisenheimer Complexes.**

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The nuclear magnetic resonance spectra of the complexes formed by reaction of methyl picrate and of 1,3,5-trinitrobenzene with potassium methoxide have been measured in solution. As a result it is possible to identify these compounds unambiguously as "Meisenheimer complexes."

THE complexes formed by the reaction of methyl picrate<sup>1</sup> and 1,3,5-trinitrobenzene<sup>2</sup> with alkali metal methoxide in methanol solution have been formulated as "Meisenheimer complexes" (I and II) on the basis of indirect evidence summarised previously.<sup>1,2</sup> (The conjugation extends to the nitro-groups although this is not explicit in the representations.)



As a result of nuclear magnetic resonance (n.m.r.) experiments, now to be described, it seems possible to remove the last remaining doubts<sup>3</sup> that these two structures indeed correspond to the complexes formed.

#### EXPERIMENTAL

Methyl picrate-potassium methoxide complex was prepared by the procedure used by Dyall.<sup>4</sup> The substance prepared by this method has the formula  $(\text{NO}_2)_3\text{C}_6\text{H}_2\cdot\text{OMe}, \text{MeOK}, \text{MeOH}$  (Found: C, 31.1; H, 3.7; K, 11.4%. Calc.: C, 31.3; H, 3.5; K, 11.3%). On being dried to constant weight *in vacuo* at 85°, there is a loss in weight of 9.5% (the calculated loss for 1 molecule of methanol being 9.3%), and the final elemental analysis corresponds to  $[(\text{NO}_2)_3\text{C}_6\text{H}_2(\text{OMe})\text{K}]$  (Found: C, 30.9; H, 2.7; K, 12.5%. Calc.: C, 30.7; H, 2.5; K, 12.5%). The loss in weight is noticeable but inconveniently slow at 80°. These results suggest the cause of a disagreement between Dyall<sup>4</sup> and Farmer.<sup>5</sup> According to Dyall, the methanol could not be removed by heating the solvated salt to 78°, whereas Farmer had reported loss of methanol to occur at 75°. 1,3,5-Trinitrobenzene-potassium methoxide complex was prepared by an exactly analogous procedure and dried *in vacuo* at room temperature.

The n.m.r. spectra of the solvated and solvent-free complexes prepared from methyl picrate in dimethyl sulphoxide were identical, except that the spectrum of the solvated complex contains additional absorption which is identical with the spectrum of methanol in dimethyl sulphoxide. This additional absorption was absent from solutions of the trinitrobenzene complex, which is accordingly inferred to be solvent-free.

The spectra were recorded at a temperature of 31° with an instrument (to be described) operating at 28 Mc./sec. Line separations relative to the proton frequency of the solvent were obtained with the aid of a precision side-band oscillator. The frequencies are reported (Table 1) in parts per million (p.p.m.) relative to an internal standard of tetramethylsilane. The solutions prepared from solid salts contained the solute at a concentration of *ca.* 1M.

\* Part VIII, *J.*, 1964, 1727.

<sup>1</sup> Gold and Rochester, *J.*, 1964, 1687.

<sup>2</sup> Gold and Rochester, *J.*, 1964, 1692.

<sup>3</sup> *E.g.*, Pollitt and Saunders, *Proc. Chem. Soc.*, 1962, 176.

<sup>4</sup> Dyall, *J.*, 1960, 5160.

<sup>5</sup> Farmer, *J.*, 1959, 3425.

TABLE I.

Chemical shifts for solutions in dimethyl sulphoxide.

(The values are expressed in p.p.m. to a precision of  $\pm 0.04$  p.p.m. relative to tetramethylsilane as internal reference. Numbers in parentheses are relative intensities of the respective lines. The intensity values for the trinitrobenzene complex are not directly comparable with the set of intensities for methyl picrate and its complex.)

Methyl picrate	-4.07 (3)	-9.07 (2)	Trinitrobenzene-potass-	-3.10 (3)	-6.14 (1) †
Methyl picrate-potassium methoxide complex	-3.03 (6)	-8.64 (2)	ium methoxide complex		-8.42 (2) ‡
Trinitrobenzene		-9.21	Methanol *		-3.14

\* Value for mean of methyl group doublet. The position of the quartet corresponding to the hydroxyl group, measured with respect to the solvent, varies with the concentration. † Broad, suggesting unresolved multiplet. ‡ Doublet.

*N.m.r. Spectra in Methanolic Sodium Methoxide.*—In spite of the resonance absorption of the solvent it is possible to observe lines at  $-9.00$  and  $-4.16$  p.p.m. for solutions of methyl picrate in methanol. As sodium methoxide is added to this solution another line (at  $-8.85$  p.p.m.) appears and, with increasing methoxide concentration, grows in intensity at the expense of the line at  $-9.00$  p.p.m. due to methyl picrate. The line at higher field becomes obscured by the solvent.

If sodium methoxide in methanol is added to a solution of trinitrobenzene in dimethyl sulphoxide, new lines at  $-6.1$  and  $-8.4$  p.p.m. appear in addition to (and gradually at the expense of) the trinitrobenzene resonance at  $-9.2$  p.p.m.

To eliminate the possibility that the phenomena observed are entirely due to specific effects of the solvents employed, some of the spectra were taken in several solvents. Substantially identical results were obtained (Table 2).

TABLE 2.

Comparison of chemical shifts in different solvents.

Species	Signal attributed to:	Solvent			
		Dimethyl-sulphoxide	Aceto-nitrile	Dimethyl-formamide	Methanol
PicOMe *	Methoxyl	-4.07	-4.07	—	-4.16
	Ring protons	-9.07	-8.92	—	-9.00
PicH	Ring protons	-9.21	-9.17	9.02	9.36
Pic(OMe) <sub>2</sub> <sup>-</sup>	Methoxyl	-3.03	-3.07	—	—
	Ring protons	-8.64	-8.78	—	-8.85
PicH(OMe) <sup>-</sup>	Methoxyl	-3.10	-3.17	-3.23	—
	3- and 5-Positions	-8.42	-8.47	-8.60	—
	1-Position	-6.14	-6.27	-6.29	—

\* Pic = 2,4,6-trinitrophenyl.

All shifts measured from internal tetramethylsilane.

The ultraviolet and visible spectra of the complexes in dimethyl sulphoxide are closely similar (maxima at 4200 and 4850—4950 Å) to those of corresponding solutions in methanol, acetonitrile, and acetone, and to those of the solutions of the parent molecules in methanolic sodium methoxide. This similarity again rules out specific chemical interaction with the solvent under our conditions.

#### DISCUSSION

The relative intensities and positions of the resonance lines are interpreted as follows. Absorptions about  $-9$  p.p.m. are associated with aromatic hydrogen atoms, those around  $-4$  p.p.m. with methoxyl groups. Both types of lines move upfield on going from the spectrum of the parent aromatic molecule to the complex, compatible with larger screening of the protons in an anionic species.

In trinitrobenzene the three aromatic hydrogen atoms are equivalent and only a single resonance is observed, but resonance in two separate regions, in the approximate intensity ratio 2 : 1, is found in the solution of the complex. The less intense signal is shifted strongly upfield towards the region of values characteristic of aliphatic hydrogen atoms, and is attributed to the unique 1-proton in formula (II). This resonance is broad; the other resonance, due to the equivalent 3- and 5-protons, appears as a doublet. These observations suggest spin-spin coupling between the latter pair of protons and the 1-proton (which now lies out of the plane of the aromatic ring) with the effect of splitting the signal from the 1-proton into a 1 : 2 : 1 triplet and the signal due to the other two ring protons into a doublet. Similar slight spin-spin coupling between the methylene and ring protons occurs in the azulonium cation.<sup>6</sup> No corresponding splitting exists in the coplanar uncharged parent systems, trinitrobenzene and azulene. In addition, there is a resonance (relative intensity 3) which is assigned to the methoxyl group. The appearance of two resonances in the intensity ratio 2 : 1 in place of the single aromatic resonance rules out proton loss from trinitrobenzene or any formulation in which the equivalence of the three aromatic hydrogen atoms is retained. It follows that complex formation must destroy the symmetry of trinitrobenzene and that the structure produced must have a life-time long enough for separate resonances of ring-protons to appear. In solutions containing both complexed and uncomplexed trinitrobenzene the appearance of spectra of both species implies that methoxide exchange between different trinitrobenzene units is not a rapid process.

The spectrum of methyl picrate contains separate resonances of nuclear and methoxyl protons. On complex formation these shift in the same direction, but the more intense resonance of methyl picrate (due to the methoxyl group) doubles in intensity. This implies either that the complex contains two equivalent methoxyl groups or else that two non-equivalent groups are in rapid equilibrium. If one were to maintain the hypothesis that this complex is due to charge-transfer interaction between methyl picrate and methoxide ions, the above observation would require the postulate that there is rapid exchange between the methoxide ions in solution and the methoxyl group attached to the ring. This postulate is disproved by the observation of discrete resonances attributable to complexed and uncomplexed methyl picrate molecules in solutions where both species are present. The slow exchange between methoxide ions and methoxyl groups accords with the spectrophotometric observation<sup>1</sup> that formation of the complex proceeds at a measurable rate. It follows, therefore, that two methoxyl groups must be firmly attached to the aromatic ring in a manner so as to preserve the equivalence of the two ring protons. Formula (I) is the only representation satisfying all these requirements.

The fact that the n.m.r. spectrum in dimethyl sulphoxide of the methyl picrate complex containing one additional molecule of methanol consists of the spectrum of the anhydrous complex together with the easily identifiable spectrum of methanol confirms that this additional methanol molecule is loosely held in the crystal and does not remain associated with a complex molecule on dissolution.

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<sup>6</sup> Danyluk and Schneider, *J. Amer. Chem. Soc.*, 1960, **82**, 997.