

215. *Meisenheimer Complexes in the m-Dinitrobenzene Series.*

By R. J. POLLITT and B. C. SAUNDERS.

The complexes obtained by the reaction of sodium methoxide with substituted 2,4- and 2,6-dinitroanisoles in solution have been examined spectroscopically. They are analogous to the Meisenheimer complexes formed by picryl ethers. A cyclic complex having a spiro-structure is described.

PICRYL ETHERS give dark red 1 : 1 complexes with alkali-metal alkoxides. Meisenheimer¹ and Jackson *et al.*² ascribed to these a structure which may be written as (I). More recent chemical evidence³ supports this type of structure, and the infrared^{3,4} and ultra-violet⁵ spectra have been determined. It has been suggested that the intermediate in activated nucleophilic aromatic substitution may resemble the Meisenheimer complex.

Less is known of similar complexes in the dinitro-series. In 1872, Salkowski⁶ obtained

¹ Meisenheimer, *Annalen*, 1902, **323**, 205.

² Jackson *et al.*, *Amer. Chem. J.*, 1900, **23**, 376; 1903, **29**, 89.

³ Dyll, *J.*, 1960, 5160.

⁴ Foster and Hammick, *J.*, 1954, 2153; Nagakura, *Tech. Rep. Inst. Solid State Physics, Tokyo*, 1962, A 35.

⁵ Foster, *Nature*, 1955, **176**, 746.

⁶ Salkowski, *Annalen*, 1872, **163**, 1.

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a colour with 4-methoxy-3,5-dinitrobenzoic acid and sodium methoxide, and from this reaction Jackson and Ittner⁷ isolated a product as an unstable solid whose analysis was correct for a 1:1 sodium methoxide:sodium 4-methoxy-3,5-dinitrobenzoate complex.

TABLE I.
Spectra of dinitroanisoles in the presence of sodium methoxide.

X	2,6-Dinitro-4-X-anisole						2,4-Dinitro-6-X-anisole					
	In MeOH			In DMF			In MeOH			In DMF		
	λ_1 (m μ)	ϵ_1/ϵ_2	λ_2 (m μ)	λ_1 (m μ)	ϵ_1/ϵ_2	λ_2 (m μ)	λ_1 (m μ)	ϵ_1/ϵ_2	λ_2 (m μ)	λ_1 (m μ)	ϵ_1/ϵ_2	λ_2 (m μ)
OMe*	—	—	—	—	—	—	—†	—	520	{ 352 365	0.60 0.57	530
Me	—†	—	618	—‡	—	626	—†	—	512	{ 350 362	0.59 0.60	518
H	—†	—	584	358§	0.05	586	—†	—	495	{ 348 353	0.54 0.52	503
Cl	—†	—	601	364	0.25	604	{ 353 365	0.64 0.59	495	368	0.85	496
SO ₃ ⁻	—†	—	560	—†	—	593	{ 356 365	0.79	484	{ 359 370	0.69 0.67	498
CO ₂ ⁻	350§	—	564	377	0.30	588	360§	—	495	{ 367 378	0.74 0.71	505
CO·NH ₂	360§	—	542	373	0.75	555	378	0.98	481	381	0.86	492
CO ₂ Me	361	0.87	526	365	0.70	532	384	1.22	472	385	0.90	486
CN	353	0.62	530	358	0.64	535	{ 376 385	1.03 1.06	469	{ 378 389	1.06 1.09	478
NO ₂	415	1.55	480	419	1.45	492	415	1.55	480	419	1.45	492

* 4-Methoxy-2,6-dinitroanisole did not give any colour with sodium methoxide in dimethylformamide or in methanol. † Any band present obscured by end-absorption. ‡ Any band present very faint. § As shoulder on end-absorption.

van de Vliet⁸ produced an intense blue solution by the action of methanolic sodium methoxide on 4-chloro-2,6-dinitroanisole; acidification gave the unchanged anisole, and the complex decomposed into a white solid when the solvent was evaporated. It appears that, unless three strongly electron-withdrawing groups are present, the complexes are stable only in solution. Other workers have mentioned various allied colour reactions of *m*-dinitro-compounds, but no systematic study has so far been made.

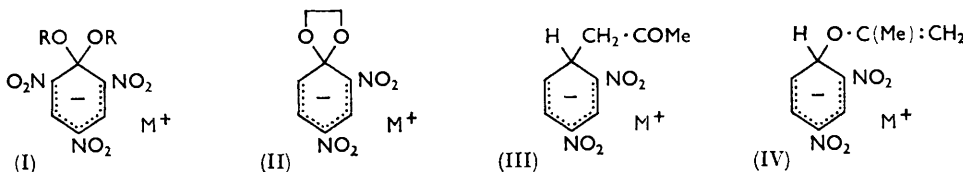
We have examined the colours obtained by the interaction of dinitroanisoles and sodium methoxide in solution. Both 2,6- and 2,4-dinitroanisoles give colours, which are formed more readily in solvents such as dimethylformamide (DMF) and dimethyl sulphoxide than in methanol. The results are summarized in Table I. In some instances the corresponding chloro-compound was used instead of the anisole, but comparison in a number of cases showed that this does not affect the final spectrum, as the halogen is rapidly replaced by methoxyl.

In general, two bands are present, one in the ultraviolet (λ_1) and the other in the visible (λ_2) region of the spectrum. In both series the long-wavelength band is progressively shifted to the blue by the introduction of increasingly electronegative substituents in the vacant 4- or 6-positions. However, there are differences between the two series, and the correlation between electronegativity and band position is by no means exact. The series converge in the trinitroanisole complex. A further regularity is seen in the short-wavelength bands (λ_1) of the 2,4-dinitroanisole complexes. As the electronegativity of the 6-substituent increases these bands move to longer wavelength and increase in intensity relative to the higher bands (λ_2). The short-wavelength band in the 2,6-dinitroanisole complexes does not seem to correspond to that in the 2,4-dinitroanisole complexes. The doublet structure which is seen in most of the latter is not present in any of the 2,6-dinitro-complexes and the wavelength of the band does not follow the electronegativity of the

⁷ Jackson and Ittner, *Amer. Chem. J.*, 1897, **19**, 199.

⁸ van de Vliet, *Rec. Trav. chim.*, 1924, **43**, 606.

4-substituent, though the intensity does so approximately. Where X = H or Me, this band is of very low intensity, or may not be present at all. Hence this (λ_1) transition seems to depend on the nature of the group in the 4-position. Where this group is kept



the same, as in the 2,4-dinitro-complexes, a regular series is seen on varying the electro-negativity of the 6-substituent.

On changing from methanol to dimethylformamide as solvent, there is a general shift to the red; this is especially large for the 4-CO₂⁻ and 4-SO₃⁻ complexes. Other solvents produce shifts which seem to be irregular and do not depend on dielectric constant. Thus,

TABLE 2.

Molar extinction coefficients, ϵ (l. moles⁻¹ cm.⁻¹), of some Meisenheimer complexes.

X	2,4-Dinitro-6-X-complex		2,6-Dinitro-4-X-complex	
	ϵ_1 *	ϵ_2	ϵ_1	ϵ_2
H	14,000	26,000 †	—	23,300
CO ₂ Me	12,700	14,100	10,600	15,200
CN ⁻	11,900 ‡	11,200	8,600	13,200
NO ₂	36,800	25,400	36,800	25,400

* Calculated for the shorter-wavelength peak where a doublet is present. † Another determination gave ϵ 26,400. ‡ 389 $m\mu$ band, ϵ 12,200.

with methyl 4-methoxy-3,5-dinitrobenzoate, the band which is situated at 532 $m\mu$ in dimethylformamide changes to 542 $m\mu$ in chloroform and 528 $m\mu$ in ether. These anomalous solvent effects may be due to fairly specific solvation of the complex. Certainly, the ease of complex-formation varies considerably with the solvent used, and in many cases removal of the solvent causes the complex to dissociate into its components.

An estimate of the molar extinction coefficients of some of these complexes was made by adding one drop of concentrated sodium methoxide solution to a standard solution of the anisole in dimethylformamide. The maximum absorption intensity of the main visible peak was determined. Under these conditions the colours fade fairly rapidly, so that the values are only approximate. The results obtained for λ_2 were then used to calculate the extinction coefficient of λ_1 . It can be seen (Table 2) that there is a steady decrease in ϵ_2 in both series as X becomes more electronegative. The trinitro-complex is anomalous in that λ_2 may be regarded as a sum of λ_2 for a 2,4-dinitro-complex and λ_2 for a 2,6-dinitro-complex. This is shown in the values for both λ_2 and ϵ_2 . The molar extinction coefficients we obtained for the trinitro-complex are somewhat higher than those given by Foster⁵ for a similar complex in acetone.

The nature of the coloured species in these solutions may be inferred both by analogy with the established Meisenheimer complex of trinitroanisole, and from the similarity of the spectra and the regular trends to the trinitroanisole spectrum in both series. Both the trinitroanisole and the methyl 4-methoxy-3,5-dinitrobenzoate complexes have been analysed directly by previous workers. A Job plot with 2,4-dinitroanisole in dimethylformamide shows that this too is a 1 : 1 complex.

Further support for this type of structure is derived from the formation of cyclic complexes using glycol ethers. Gitis and Kaminskii⁹ record a value of λ_{max} 493 $m\mu$ for the reaction of glycol 2,4-dinitrophenyl ether with acetone and sodium hydroxide solution.

⁹ Gitis and Kaminskii, *Zhur. obshchei Khim.*, 1960, **30**, 3810.

This is far too low for the expected Janovsky complex; 2,4-dinitroanisole gives λ_{\max} 560 $m\mu$ and 2,4-dinitrophenetole 561 $m\mu$.⁹ This spectrum, then, is almost certainly due to an internal Meisenheimer complex (II). Glycol 2,4-dinitrophenyl ether gives the characteristic salmon-pink colour of a compound absorbing at about 490 $m\mu$ in the presence of alkali. In dimethylformamide, in the presence of sodium hydroxide solution, the complex seems to be formed almost quantitatively, with maxima at 345, 355, and 500 $m\mu$, of relative intensities 0.51, 0.51, and 1.0, and no other absorption above 265 $m\mu$ where the solvent cut-off occurs. These cyclic complexes can be isolated as solids.

Structures (III) and (IV), which are very similar to that of the Meisenheimer complex, have been suggested¹⁰ for the coloured products of the well-known Janovsky reaction. While the general features of the spectra of both the Janovsky and the Meisenheimer complexes are similar, the difference in wavelength of the visible peaks (*m*-dinitrobenzene gives λ_{\max} 576 $m\mu$ in alkaline acetone) requires some further explanation. The detailed structure of the Janovsky complex will be dealt with in a later publication.

EXPERIMENTAL

The spectra were determined using a Perkin-Elmer model 137 ultraviolet spectrophotometer. As many of the peaks are broad, and some of the solutions fade rapidly, the limit of accuracy of the values given is $\pm 2 m\mu$. For the determination of extinction coefficients, a Unicam S.P. 500 spectrophotometer was used.

Methanol was used without further purification. The dimethylformamide was fractionated under reduced pressure to remove free dimethylamine; a sample successfully purified in this way gave a virtually colourless solution with 1,3,5-trinitrobenzene. With the exception of the nitriles, the nitro-compounds were made by established methods, and had melting points which agreed with literature values.

2-Chloro-3,5-dinitrobenzotrile.—This was prepared from the corresponding amide and phosphorus pentachloride, following a method similar to that of Kirsanov and Makitra.¹¹ The intermediate phosphoramidic trichloride was rather stable, but decomposed smoothly on being heated at 190° for 3 hr., to give the product, m. p. 138° (lit.,¹² 139°).

4-Chloro-3,5-dinitrobenzotrile.—A similar method to the above was used, the intermediate being heated at 160° for 20 min. Two recrystallizations from ethanol gave the pure *nitrile*, m. p. 141.5° (Found: C, 37.15; H, 1.1; N, 18.9. $C_7H_2ClN_3O_4$ requires C, 36.9; H, 0.9; N, 18.5%). This was converted by methanolic sodium methoxide into 4-methoxy-3,5-dinitrobenzotrile, m. p. 114° (lit.,¹³ 114°).

Preparations of Complexes.—In *dimethylformamide*. To a solution (10 ml.) of the nitro-compound in dimethylformamide (ca. 1 mg./ml.) was added 1—2 small drops (0.01 ml.) of 10% methanolic sodium methoxide. This gave an intensely coloured solution which was diluted a few hundred-fold with dry dimethylformamide for spectroscopic examination.

In methanol. For this about 20 mg./ml. of the nitro-compound must be used. It is necessary to add up to an equal volume of 10% sodium methoxide solution to give an intense colour.

In both solvents less of the nitro-compound was required when it had an electron-withdrawing 5-substituent, and considerably more when it had an electron-donating 5-substituent.

Determination of Extinction Coefficients.—Standard solutions of the nitro-compounds were made up in dimethylformamide and diluted so that the complex gave a suitable optical density in a 1 mm. or 2 mm. cell. A drop (0.01 ml.) of concentrated methanolic sodium methoxide solution was added to the solution in the cell, and the optical density at λ_2 was determined at short intervals until it reached a maximum. Repetition of the experiment with three times the quantity of sodium methoxide gave similar values.

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UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

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¹⁰ Canbach, *Farm. Revy.*, 1949, **48**, 153; Gitis, *Zhur. obshchei Khim.*, 1957, **27**, 1894.

¹¹ Kirsanov and Makitra, *Zhur. obshchei Khim.*, 1956, **26**, 907.

¹² Blanksma, *Rec. Trav. chim.*, 1901, **20**, 411.

¹³ Blanksma and Whitte, *Rec. Trav. chim.*, 1941, **60**, 811.