

Colour Effects with the Nitrobenzyl Esters of Dimethylaminobenzoic Acids

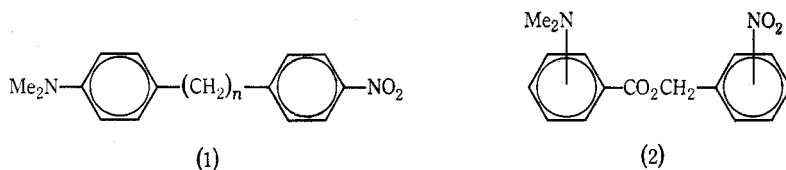
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Abstract

Nitrobenzyl esters of dimethylaminobenzoic acids are strongly coloured in the solid state but not in solution. The operation of electron donor-acceptor interaction within the crystal lattice is indicated. One of the compounds, *o*-nitrobenzyl *m*-dimethylaminobenzoate, formed two differently coloured polymorphic modifications.

Substituted diphenylalkanes (1) exhibit electron donor-acceptor interaction in solution, resulting in marked bathochromic shifts and intensity enhancement of the ultraviolet absorption maxima with development of colour.^{1,2} The present communication reports some colour effects which have been observed with certain compounds of related general structure (2), namely, the nitrobenzyl esters of dimethylaminobenzoic acids. New derivatives of this type were being investigated in connection with the pH-dependent fluorescence of *m*-dimethylaminobenzoic acid and its possible use in small protein-structure probes.



The *m*- and *p*-nitrobenzyl esters of *m*-dimethylaminobenzoic acid formed orange-red and deep orange crystals, respectively, whilst the *o*-, *m*- and *p*-esters of *p*-dimethylaminobenzoic acid were various shades of yellow. In the case of *o*-nitrobenzyl *m*-dimethylaminobenzoate, however, two readily interconvertible orange and yellow polymorphic forms were obtained according to the conditions of crystallization. The orange form was also converted into the other on heating. The modifications had significantly different infrared spectra in KBr. Although colour formation as a result of electron donor-acceptor interaction, as exemplified by compounds (1) and (2), is fairly widespread in organic chemistry,³ the association of

¹ White, W. N., *J. Am. Chem. Soc.*, 1959, **81**, 2912.

² Glushenkov, V. A., Izmail'skii, V. A., and Moshkovskii, Yu. Sh., *Dokl. Phys. Chem.*, 1963, **153**, 1125.

³ Foster, R., 'Organic Charge Transfer Complexes' p. 1 (Academic Press: New York 1969).

apparently different levels of interaction with polymorphic states of a compound appears to be unique. Crystallographic analysis of both coloured forms of this ester could clearly be of interest.

In contrast to the diphenylalkanes (1), the ultraviolet spectra of the esters (2) were essentially additive with respect to the separate aromatic moieties, and showed no absorption in the visible region, so that the electronic effect in the present series is apparently confined to the crystal lattice.*

Nitrile groups often occur in electron acceptor components,³ and for this reason *o*-cyanobenzyl *m*-dimethylaminobenzoate was also prepared, but it did not exhibit any exceptional colour behaviour.

Experimental

Microanalyses were carried out by the Australian Microanalytical Service, Melbourne. Melting points are uncorrected. Infrared spectra were obtained with KBr discs, and ultraviolet spectra were recorded on methanol solutions.

Preparation of Substituted Benzyl Dimethylaminobenzoates

A solution of the acid and triethylamine (1 equiv.) in dimethylformamide (c. 2 M) was treated with the appropriate benzyl chloride or bromide and kept overnight at room temperature. Dilution with water gave the ester, which was washed with water and cold ethanol. The following products were recrystallized from ethanol.

p-Nitrobenzyl *m*-dimethylaminobenzoate (81% yield) formed deep orange prisms, m.p. 111.5–112.5° (Found: C, 64.2; H, 5.4; N, 9.2. $C_{16}H_{16}N_2O_4$ requires C, 64.0; H, 5.3; N, 9.3%).

m-Nitrobenzyl *m*-dimethylaminobenzoate (70% yield) formed orange-red needles, m.p. 69–70° (Found: C, 64.1; H, 5.3; N, 9.3%).

o-Nitrobenzyl *m*-dimethylaminobenzoate (71% yield) formed bright yellow laths on slow recrystallization, m.p. 95.5–96° (Found: C, 64.2; H, 5.4; N, 9.1%). Rapid crystallization produced orange needles (Found: C, 63.9; H, 5.6; N, 9.5%), which were converted into the yellow modification on heating to c. 86°. This transformation was confirmed by the infrared spectra which were substantially different for the two polymorphic forms, particularly in the 800–1400 cm^{-1} region. The ester carbonyl band was at the same position (1727 cm^{-1}) in both forms, but was appreciably broader in the case of the yellow material.

p-Nitrobenzyl *p*-dimethylaminobenzoate (81% yield) formed deep yellow needles, m.p. 131.5–132.5° (Found: C, 64.3; H, 5.5; N, 9.4%).

m-Nitrobenzyl *p*-dimethylaminobenzoate (83% yield) formed yellow needles, m.p. 126–127° (Found: C, 63.9; H, 5.3; N, 9.3%).

o-Nitrobenzyl *p*-dimethylaminobenzoate (72% yield) formed light yellow laths, m.p. 103–104° (Found: C, 64.0; H, 5.5; N, 9.3%).

o-Cyanobenzyl *m*-dimethylaminobenzoate (86% yield) formed colourless prisms, m.p. 88–88.5° (Found: C, 73.0; H, 5.7; N, 10.1. $C_{17}H_{16}N_2O_2$ requires C, 72.9; H, 5.7; N, 10.0%).

2,4,6-Trimethylbenzyl *m*-dimethylaminobenzoate (90% yield) formed colourless prisms with a strong blue fluorescence, m.p. 124.5–125° (Found: C, 76.9; H, 7.7; N, 4.5. $C_{19}H_{23}NO_2$ requires C, 76.8; H, 7.7; N, 4.7%).

Acknowledgment

The author is indebted to Mr P. A. Hoyne for technical assistance.

Manuscript received 22 December 1977

* 2,4,6-Trimethylbenzyl *m*-dimethylaminobenzoate served as a colourless spectroscopic reference compound.