

An anomalous chromatographic behaviour of some di- and trinitrophenols

In a previous communication¹ a paper chromatographic method for the separation and identification of variously substituted mono-, di- and trinitrophenols has been described. Recently we have had the opportunity to chromatograph some further derivatives and have found that some di- and trinitro-derivatives of alkylphenols showed an anomalous behaviour.

Experimental

Materials. The preparation of 4,6-dinitro-2,5-xyleneol has been described in a previous communication². Its identity was confirmed by melting point determination and elementary analysis. 4,6-Dinitro-3,5-xyleneol was prepared by nitration according to ROWE *et al.*³ and had a m.p. of 114–115° (according to ref. 3, 115–116°). 4,6-Dinitro-2,3-xyleneol was prepared by nitration of 2,3-xyleneol with nitrous acid² and had a m.p. of 83.5–84° (according to ref. 4, 86°). 4,6-Dinitro-2-*tert.*-butyl-5-methylphenol was prepared according to the literature⁵ and had a m.p. of 106–107° (according to ref. 5, 107–108°). Other nitrophenols have been described in previous communications^{1,2}.

Paper chromatography. Paper chromatography was carried out in the same manner as previously¹, *i.e.* use was made of the solvent system 1-bromonaphthalene–80 % acetic acid.

Absorption spectra. Absorption spectra were determined in the same manner as described previously⁶.

Results and discussion

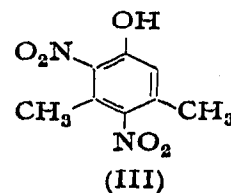
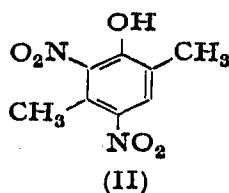
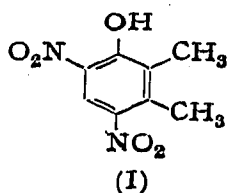
In the previous communication¹ we calculated the ΔR_M values for the individual functional groups, *e.g.* for the methyl group *meta* to the hydroxygroup the ΔR_M value was +0.23, for the methyl group *ortho* to the hydroxygroup +0.33.

In Table I the calculated and observed R_F values of the newly chromatographed

TABLE I
OBSERVED AND CALCULATED R_F VALUES OF SOME NITROPHENOLS

Nitrophenol	R_F observed	R_F calculated
4,6-Dinitrophenol	0.39	—
4,6-Dinitro- <i>o</i> -cresol	0.20	0.23
4,6-Dinitro- <i>m</i> -cresol	0.28	0.27
4,6-Dinitro-2,3-xyleneol	0.12	0.15
4,6-Dinitro-2,5-xyleneol	0.59	0.15!
4,6-Dinitro-3,5-xyleneol	0.67	0.12!
4,6-Dinitro-2- <i>tert.</i> -butylphenol	0.10	—
4,6-Dinitro-2- <i>tert.</i> -butyl-5-methylphenol	0.32	0.06!
4-Nitro-2,5-xyleneol	0.76	—
2,4,6-Trinitrophenol	0.55	—
2,4,6-Trinitro- <i>m</i> -cresol	0.39	0.42
2,4,6-Trinitro-3,5-xyleneol	0.56	0.30!

nitrophenols are summarized. At first sight, in the case of 4,6-dinitrophenols, the calculated R_F values of *o*- and *m*-cresol and 2,3-xylene derivatives show a satisfactory agreement with the observed values. In the case of the dinitro-derivatives of 2,5- and 3,5-xylenols, however, they differ considerably. As expected, in comparison with 4,6-dinitrophenol the corresponding derivatives of *o*- and *m*-cresol have lower R_F values, the derivative of 2,3-xylene (I) a still lower value and the derivative of 2-*tert.*-butylphenol the lowest R_F value. Rather surprisingly the derivatives of 2,5- and 3,5-xylenols (II and III) have R_F values greater than the unsubstituted 4,6-dinitrophenol. Their behaviour on the chromatogram is very similar to that of *p*-nitrophenols. The R_F value of one corresponding *p*-nitrophenol is, for comparison, recorded in Table I. The behaviour of 4,6-dinitro-2-*tert.*-butyl-*m*-cresol is analogous. This compound has a higher R_F value than 4,6-dinitro-2-*tert.*-butylphenol, though owing to the presence of the methyl group it should have a lower R_F value.



From the example mentioned it can be deduced that the behaviour of dinitrophenols is anomalous where a methyl group is present in the position between the two nitro groups. When studying the molecular model we found that, in this case, all the three substituents are no longer coplanar with the benzene nucleus and that one of the nitro groups is forced out of coplanarity. 4,6-Dinitro-3,5-xylene has a greater R_F value than 4,6-dinitro-2,5-xylene. The difference in their R_F values corresponds to that of the dinitro-derivatives of *o*- and *m*-cresol. Because the anomalous dinitrophenols behave on the chromatogram like *p*-nitrophenols, it may be deduced that the nitro group forced out of coplanarity is that in the *ortho*-position. This, of course, essentially changes the properties and the character of the original molecule, resulting also in changes in chromatographic behaviour. Assuming that displacement of the *o*-nitro group from coplanarity could also affect the hydrogen bonding between the hydroxy and nitro groups, higher R_F values of the anomalously behaving phenols would be obtained. In the case of 2,4,6-trinitrophenols the same anomalous behaviour is shown only in the presence of two methyl groups in the molecules. In 2,4,6-trinitro-*m*-cresol one *o*-nitro group still remains for the hydrogen bonding and therefore this compound does not behave anomalously.

In connection with other work⁶ we determined the absorption spectra of those compounds in their yellow alkaline solutions. All 4,6-dinitrophenols have characteristic spectra with 2 maxima at *ca.* 375–380 and 400–420 $m\mu$, whereas *p*-nitrophenols show only 1 maximum at 408–415 $m\mu$ (Fig. 1). The spectra of both nitrophenols showing the anomalous chromatographic behaviour are very similar to that of *p*-nitrophenol. In this case, probably, the non-coplanarity has some influence on the electronic states of the molecules. Similar effects of the alkyl groups on the absorption spectra of trinitrobenzenes have been ascribed recently to steric inhibition of resonance and steric enhancement of resonance⁷. Although all these phenomena cannot be directly compared it is evident that in all cases the steric effects play the main role.

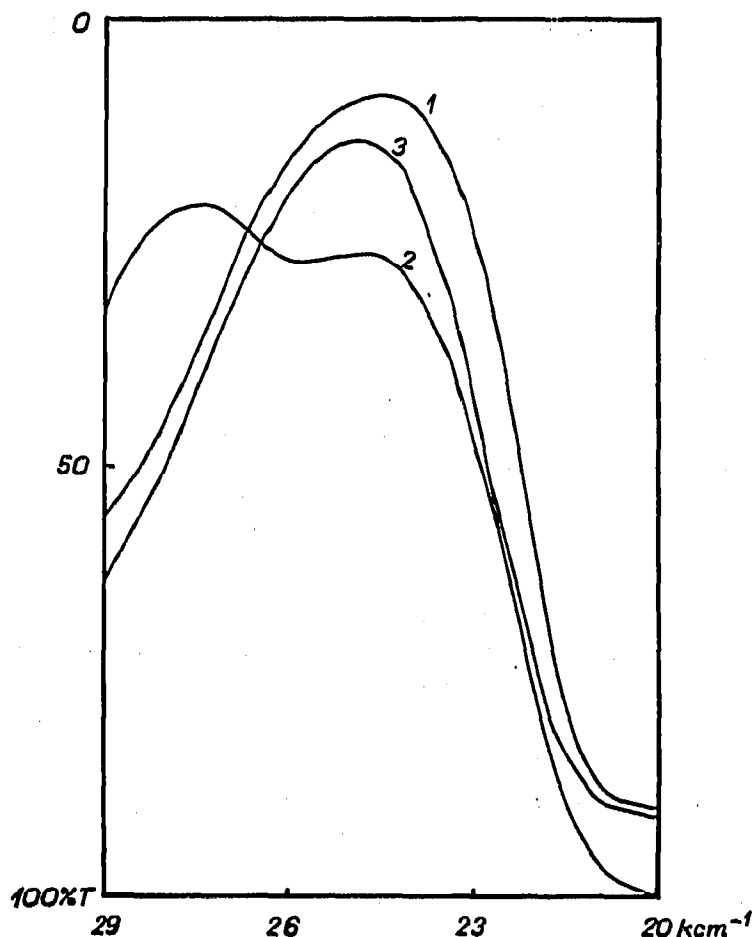


Fig. 1. Absorption spectra of the nitrophenols in ethanolic ammonia. (1) 4-Nitrophenol; (2) 4,6-dinitrophenol; (3) 4,6-dinitro-2,5-xyleneol.

These facts illustrate that steric factors may have a considerable effect on the chromatographic behaviour of organic compounds at least if they interfere with the formation of hydrogen bonds. In the case of small molecules with many and/or bulky substituents care must therefore be taken when calculating the theoretical R_F values from the ΔR_M data. Attention should also be paid to possible interactions of those groups and their effect on the character of the whole molecule.

Research Institute for Organic Syntheses,
Pardubice-Rybitví (Czechoslovakia)

J. GASPARIČ

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