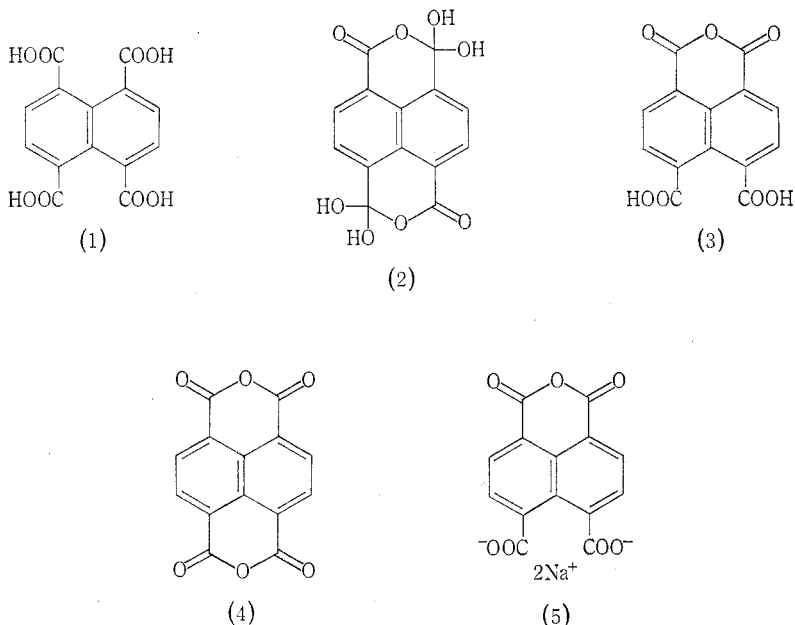


SPECIES EXISTING IN SOLUTIONS OF NAPHTHALENE-1,4,5,8-TETRACARBOXYLIC ACID

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Naphthalene-1,4,5,8-tetracarboxylic acid (1) is commercially available at relatively low cost, and it is the precursor of important orange and red vat dyes of the bis-benzimidazole type.¹ There have been few reports on its chemistry other than those connected with dyestuffs or those in which it is identified as an oxidation product of polycyclic aromatic hydrocarbons.² We report here an infrared and proton magnetic resonance (p.m.r.) spectroscopic study of the tetraacid and some of its salts, and our interpretation of the spectroscopic data in terms of equilibria among the tetraacid, its anhydrides, and the carboxylate anions.



The tetraacid (1) dissolves readily in dimethyl sulphoxide at room temperature, and the p.m.r. spectrum of this solution shows the aromatic proton resonances as an

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¹ Venkataraman, K., "The Chemistry of Synthetic Dyes." Vol. II, p. 1191. (Academic Press: New York 1952.)

² Rodd, E. H., (Ed.), "Chemistry of Carbon Compounds." Vol. III, p. 1333. (Elsevier: Amsterdam 1956.)

AB quartet, δ_A 8.60, δ_B 8.23 (J_{AB} 7.6 Hz). Magnetic non-equivalence in each pair of aromatic protons implies a dissymmetry which could arise from the existence of the tetraacid in the pseudo-acid form (2). Alternatively, the solute giving rise to the p.m.r. spectrum might be the monoanhydride (3) and not the tetraacid. Dehydration of (1) into (3) would also produce a mole of water but, since no OH resonances were observable in the dimethyl sulphoxide solutions of the tetraacid, this basis for choice between (2) and (3) was not available. However, the infrared spectrum of the solution showed a strong carbonyl absorption at 1765 cm^{-1} which clearly implicates the monoanhydride (3). The pseudo-acid (2) might be expected to show a carbonyl absorption frequency close to that observed³ for the δ -lactone naphthalide (1727 cm^{-1}). The use of dimethyl sulphoxide as a solvent for infrared spectroscopy requires some comment. The high frequency end of the normal carbonyl stretching region is accessible down to 1725 cm^{-1} . In this solvent, naphthalene-1,8,4,5-tetracarboxylic dianhydride (4) shows infrared absorption at 1780 and 1765 cm^{-1} and naphthalene-1,8-dicarboxylic anhydride at 1770 and 1732 cm^{-1} , only slightly different from the values observed for Nujol mulls.

The commercially available tetraacid (1) certainly exists as such, as evidenced by its elementary analysis. The infrared absorption of a Nujol mull shows a peak at 1729 cm^{-1} but no sign of the higher frequency absorption expected of an anhydride. By way of contrast, naphthalene-1,8-dicarboxylic acid, when stored, slowly loses water to form the anhydride, and we were unable to examine the 4,5-dinitro- and 4,5-dichloro-naphthalene-1,8-dicarboxylic acids due to their rapid, spontaneous conversion into the anhydrides. The monoanhydride (3), once formed, also appears to be moderately stable. Dilution of the dimethyl sulphoxide solution with water precipitates solid (3) which has diagnostic carbonyl absorptions (in Nujol) at 1765 and 1735 cm^{-1} ; microanalytical data for the solid were sufficiently accurate to confirm its identity.

The p.m.r. spectrum of the dimethyl sulphoxide solution of the monoanhydride (3) undergoes some informative changes when the sample is heated in the probe. Above 80° , a sharp singlet appears in the spectrum at 8.74 p.p.m. and its intensity increases as the temperature is raised further. At the same time, the intensity of the AB quartet is reduced and it is evident that the responsible solutes are in equilibrium between 100° and 140° . Below 100° , equilibration is very slow and rapid cooling freezes the equilibrium so that the new substance crystallizes from solution. It is easily recovered and identified as the dianhydride (4) by means of its infrared spectrum. The chemical shift of the aromatic protons is strongly affected by the coplanar carbonyl groups and resembles that of the low field pair in the monoanhydride (3). Tetraacid (1) (60 mg) dissolved in dimethyl sulphoxide (1.00 ml) is approximately 45% converted into bisanhydride at 100° , and 70% converted at 140° . Dissolving the pure anhydride in moist dimethyl sulphoxide and heating above 100° also serves to establish the equilibrium. As far as we are aware, this is a unique occasion when the equilibrium between a diacid and its cyclic anhydride may be observed.

When the tetraacid (1) is dissolved in water with two moles of sodium hydroxide, the solution soon deposits fine brown needles of the disodium salt. However, the

³ Corran, J. A., and Whalley, W. B., *J. chem. Soc.*, 1958, 4719.

supersaturated solution prior to crystallization, the supernatant after crystallization, and solutions made by redissolving the disodium salt, all show p.m.r. evidence for two species in solutions. The major species gives rise to a single resonance at δ 7.73 and is believed to be a dianion of the tetraacid in which rapid proton exchange produces high pseudo-symmetry. The minor species gives rise to a pair of doublets (J 7 Hz) at δ 7.94 and 8.60. Because of its larger chemical shift we assign the low-field doublet to the protons *ortho* to the anhydride carbonyls in the species (5), which must be in equilibrium with the regular dianion. Similar spectra were observed for solutions of the tetraacid and sodium carbonate but, in this case, the crystalline solid appeared to contain some carbonate and good analytical data could not be obtained.

In the presence of excess sodium carbonate, the tetraanion is presumably formed, and a singlet at δ 7.68 is observed in the p.m.r. spectrum. The tetrasodium salt is also formed in solutions of the tetraacid with four moles of sodium hydroxide. It can be isolated by precipitation with alcohol, and when redissolved in deuterium oxide gives rise to a single p.m.r. resonance at δ 7.68.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 257 infrared spectrometer. P.m.r. spectra were measured on a Varian A56/60 spectrometer operating with a normal probe temperature of approximately 44°; chemical shifts are quoted relative to Tiers's salt⁴ as internal standard. Elementary analyses were performed by the Australian Microanalytical Service, Melbourne. None of the compounds reported in this work had a definite melting point.

Naphthalene-1,4,5,8-tetracarboxylic Acid (1)

The acid was purchased from the Aldrich Chemical Company (Found: C, 55.1; H, 2.4. $C_{14}H_8O_8$ requires C, 55.3; H, 2.7%).

Naphthalene-1,4,5,8-tetracarboxylic Acid 1,8-Anhydride (3)

The tetraacid (1) (0.50 g) was dissolved in dimethyl sulphoxide (5 ml) at room temperature. Water (20 ml) was then added, and the precipitated solid was filtered off and washed well with water. After the product had been left to dry in air for several days, a sample was submitted for analysis (Found: C, 57.9; H, 2.3. $C_{14}H_6O_7$ requires C, 58.8; H, 2.1%).

Disodium Salt of Naphthalene-1,4,5,8-tetracarboxylic Acid

Tetraacid (1) (380 mg, 1.25 mmol) and sodium hydroxide (100 mg, 2.50 mmol) were dissolved together in water (2.0 ml). The solution was left for a few days and the crystallized product was collected, washed with a little water, and dried (Found: C, 48.1; H, 1.9; sulphated ash, 38.9. $C_{14}H_6Na_2O_8$ requires C, 48.3; H, 1.7; sulphated ash, 40.8%).

Tetrasodium Salt of Naphthalene-1,4,5,8-tetracarboxylic Acid

Tetraacid (1) (380 mg, 1.25 mol) and sodium hydroxide (200 mg, 5.0 mol) were dissolved in water (5 ml). The solution was filtered and added dropwise to hot ethanol (10 ml) to precipitate the salt. The mixture was filtered and the precipitate was washed well with ethanol and then dried in air. The *tetrasodium salt* was a buff-coloured solid which retained water tenaciously, even after prolonged drying (Found: C, 40.0; H, 1.9; sulphated ash, 65.6. $C_{14}H_4Na_4O_8 \cdot 2H_2O$ requires C, 39.3; H, 1.9; sulphated ash, 66.4%).

⁴ Emsley, J. W., Feeney, J., and Sutcliffe, L. H., "High Resolution Nuclear Magnetic Resonance Spectroscopy." Vol. 1, 265. (Pergamon: Oxford 1965.)