

THE LOW STRENGTH OF HIGHLY HINDERED AROMATIC CARBOXYLIC ACIDS

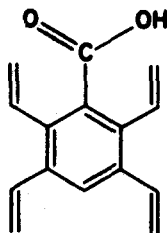
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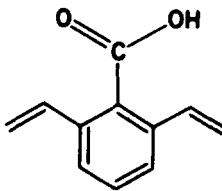
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o-TOLUIC acid ($10^5K = 12.35$)¹ is stronger than benzoic acid ($10^5K = 6.27$)¹. 2,3-Dimethylbenzoic acid is stronger still ($10^5K = 18.7$) due to buttressing². 2,6-Dimethylbenzoic acid is very strong ($10^5K = 56.8$)² but the double buttressing in 2,3,5,6-tetramethylbenzoic acid leads surprisingly to lower strength ($10^5K = 37$)³ for which an explanation was advanced⁴. A similar decrease in strength has now been found on passing from 2,6-diisopropylbenzoic acid ($10^5K = 65$) to 2,3,5,6-tetraisopropylbenzoic acid ($10^5K = 7$).

Hindrance in the latter tetra acid must be very high. The constituent methyl groups of adjacent isopropyl groups will be forced outwards to impinge closely on the carboxyl groups (I) a situation not



I



II

¹J.F.J. Dippy, Chem. Rev. **25**, 151 (1939)

²J.F.J. Dippy, S.R.C. Hughes and J.W. Laxton, J. Chem. Soc. 1470 (1954)

³M. Crawford and J.H. Magill, Trans. Faraday Soc. **51**, 704 (1955)

⁴M. Crawford and F.H.C. Stewart, Trans. Faraday Soc. **49**, 752 (1953)

occurring in 2,6-diisopropylbenzoic acid (II). Despite the great hindrance this tetra acid is almost as weak as benzoic acid. 2,4,6-Tri-*t*-butylbenzoic acid, another highly hindered acid, was found to be even weaker than benzoic acid⁵. Thus moderate steric hindrance strengthens an acid but intense steric hindrance leads to weakening.

Steric hindrance of solvation of the carboxylate ion has been held responsible for low strength in hindered aliphatic acids⁶ and hindered diterpenoid acids^{7,8}. The low strength of one of these acids said to be the most hindered known⁸ is associated with shielding of the carboxyl.

Resulting from steric compression, distortion of the carboxyl group with alteration of the OCO angle and CO distances might impair carboxylic resonance and weaken an acid. Examination of the infrared spectra of benzoic acid, 2-methyl-, 2,6-dimethyl-, 2,4,6-trimethyl-, 2,4,6-triisopropyl-, 2,3,5,6-tetramethyl- and 2,3,5,6-tetraisopropylbenzoic acids and their methyl esters revealed no irregularities except that in 2,3,5,6-tetraisopropylbenzoic acid there is a distinct doublet ($\nu_{\text{CO}} = 1741, 1748$; $\epsilon^{\text{a}} = 300, 255$) at the frequency expected for the carboxyl bond in the monomer. A similar doubling is present to a lesser extent in 2,3,5,6-tetramethylbenzoic acid ($\nu_{\text{CO}} = 1737, 1750$; $\epsilon^{\text{a}} = \text{ca. } 80, 325$). This indicates steric compression as it may be due to constraint of the carboxyl group into two different conformational structures but it does not appear in the esters. An abnormally

⁵E.E. Betts and L.R.C. Barclay, Canad. J. Chem. **33**, 1768 (1955)

⁶G.S. Hammond and D.H. Hogle, J. Amer. Chem. Soc. **77**, 338 (1955)

⁷O.E. Edwards and R. Howe, Proc. Chem. Soc. **77**, 338 (1959)

⁸J.W. ApSimon, O.E. Edwards and R. Howe, Canad. J. Chem. **40**, 630 (1962)

low value (1690 cm^{-1}) for the CO stretching frequency of ApSimon, Edwards and Howe's acid was observed⁸.

The solubilities of 2,6-di- and 2,3,5,6-tetra-isopropylbenzoic acid in water are very low and it has been necessary to carry out the determinations of the dissociation constants (classical) in various strengths of aqueous ethanol. A spectrophotometric method³ has been used. With benzoic acid Grunwald⁹ obtained an almost linear relationship between pK' and ethanol concentration below about 70% ethanol-water (w/w). We have confirmed this and find that it also holds good for the above acids within the range measured. One can thus extrapolate to 0% ethanol and obtain their pK values in water (see Table).

pK' Values in Aqueous Ethanol

	% Ethanol							
	0	7.7	21.9	40.5	43.8	49.3	64.4	69.1
2,6-diisopropylbenzoic acid	3.19*	3.55	4.24	5.13			5.99	
2,3,5,6-tetraisopropylbenzoic acid	4.15*				5.48	5.62		6.22

*extrapolated

Details of the determinations and of the preparation of the hitherto unknown 2,6-diisopropylbenzoic acid will be given elsewhere.

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⁹E. Grunwald and B.J. Borkowitz, J. Amer. Chem. Soc. **73**, 4939 (1951)

¹⁰J. Thiec, Ann. Chim. (France) **9**, 51 (1954)