

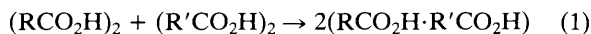
Isolation and Characterization of 1 : 1 Crystalline Substituted Benzoic Acid Heterodimers resulting from Intermolecular Hydrogen Bonding

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Eighteen crystalline benzoic acid heterodimers have been prepared for the first time and characterized by elemental analyses, ^1H n.m.r. and i.r. spectra, m.p./composition phase studies, and X-ray powder diffraction.

Hydrogen bonding in carboxylic acids has been widely investigated¹ in gaseous, liquid, solid, and solution phases. Since the first postulation of hydrogen-bonded carboxylic acid dimers by Pfeiffer² in 1914, the presence of dimers resulting from hydrogen bonding between carboxy groups has been experimentally demonstrated in all these phases. However, only occasional studies have been carried out on interactions between different carboxylic acids. Thus, for example, Christian *et al.*³ presented i.r. evidence for the formation of heterodimers (equation 1) between trichloroacetic and acetic



acids in CCl_4 and for trifluoroacetic and acetic acids using vapour-phase studies.⁴ Kohler *et al.*⁵ found evidence for formation of a solid heterodimer between trifluoroacetic and acetic acids in phase studies. In a study involving i.r. and n.m.r. spectra of trifluoroacetic and trimethylacetic acids in inert solvents at low temperatures (-120 to -170°C), Golubev and Denisov⁶ reported separate ^1H n.m.r. signals which they attributed to two non-equivalent protons resulting from slow exchange. Desiraju *et al.*⁷ reported the isolation of a solid heterodimer of cinnamic acids in connection with their crystal engineering photochemical studies.

Stable heterodimers of substituted benzoic acids in the present investigation were prepared by dissolving equimolar amounts of the two acids in hot 95% ethanol and allowing crystals to form which were then recrystallized to a constant melting point. X-Ray powder diffraction patterns of the heterodimers differed from those of the component acids and did not show any peaks for the strongest lines of the component acids. Evidence for a 1:1 stoichiometry of component acids in the heterodimers was from ^1H n.m.r. determinations of their solutions in $[\text{D}_6]\text{acetone}$. Integration of appropriate signals showed a 1:1 ratio accurately and the two carboxy protons as a singlet with a relative area of 2. Additional evidence for a 1:1 stoichiometry was from elemental analyses and from an m.p./composition phase study which showed formation of the heterodimer at the 0.5 mol ratio for one of the heterodimers (5). The i.r. spectra (mineral oil mull) of the heterodimers in general were more complex than those of the component acids and showed broad OH and C=O stretching bands in regions close to those of the component acids.

The 18 heterodimers prepared are listed in Table 1. Several others were obtained as mixtures with their component acids as indicated by the presence of lines in the X-ray powder diffraction patterns from all three components. In several other combinations attempted (for example, 3,5-dinitrobenzoic acid with benzoic acid, 3-methylbenzoic, 4-methoxybenzoic, and 3,5-dimethoxybenzoic acids), only lines of the two original acids appeared in the X-ray powder diffraction patterns.

It can be noted that for the formation of stable heterodimers, one ring must be substituted by one or more

Table 1. Benzoic acid heterodimers.

Compound	Substituents
(1)	3,4-dinitro/2,4-dimethoxy
(2)	3,4-dinitro/2,6-dimethoxy
(3)	3,4-dinitro/3,4-dimethoxy
(4)	3,4-dinitro/2,6-dimethyl
(5)	3,4-dinitro/2,4,6-trimethyl
(6)	3,5-dinitro/2,6-dimethoxy
(7)	3,5-dinitro/2,6-dimethyl
(8)	3,5-dinitro/3,4-dimethoxy
(9)	3,5-dinitro/2,4,6-trimethyl
(10)	3,5-dinitro-2-methyl/2,4-dimethoxy
(11)	3,5-dinitro-2-methyl/3,4-dimethoxy
(12)	2,4-dichloro/3,4-dimethoxy
(13)	2,5-dichloro/2,4-dimethoxy
(14)	2,6-dichloro/2,4-dimethoxy
(15)	3,5-dinitro/2,4-dimethoxy
(16)	3,5-dinitro/4-t-butyl
(17)	4-nitro/4-methyl
(18)	4-nitro/4-methoxy

electron-withdrawing groups such as nitro or chloro and the other ring by electron-donating groups such as methoxy and alkyl. This investigation opens up possibilities for investigations of many other combinations using other types of electron-withdrawing and -donating groups as well as further studies with the heterodimers.

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References

- G. C. Pimentel and A. L. McClellan, 'The Hydrogen Bond,' Freeman & Co, San Francisco, 1960, pp. 253, 265, 268; M. D. Joesten and J. J. Schaad, 'Hydrogen Bonding,' Marcel Dekker, New York, 1974, pp. 1ff; E. Lippert, Ch. 1 in 'The Hydrogen Bond. Recent Developments in Theory and Experiments,' Vol. 1, Theory, eds. P. Schuster, G. Zundel, and C. Sandorfy, North-Holland Publishing Co., New York, 1976, pp. 5ff.
- P. Pfeiffer, *Ber.*, 1914, **47**, 1580.
- H. E. Affsprung, S. D. Christian, and A. M. Melnick, *Spectrochim. Acta*, 1964, **20**, 285.
- S. D. Christian, H. E. Affsprung, and C. Ling, *J. Chem. Soc.*, 1965, 2378; S. D. Christian, H. E. Affsprung, and R. W. Gray, *J. Chem. Soc. (A)*, 1966, 293.
- F. Kohler, G. H. Findenegg, and M. Bobik, *J. Phys. Chem.*, 1974, **78**, 1709.
- N. S. Golubev and G. S. Denisov, *Zh. Prikl. Spektrosk.*, 1982, **37**, 265.
- G. R. Desiraju, R. Kamala, B. Kumari, and J. A. R. P. Sarma, *J. Chem. Soc., Perkin Trans. 2*, 1984, 181; G. Desiraju and J. A. R. P. Sarma, *J. Chem. Soc., Chem. Commun.*, 1983, 45.