

SHORT COMMUNICATIONS

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The C—O vs O—H length correlation in hydrogen-bonded carboxyl groups. By MIZUHIKO ICHIKAWA, *Department of Physics, Faculty of Science, Hokkaido University, Sapporo 060, Japan*

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Abstract

The correlations between the bond length and angle at a donor O atom and the hydrogen-bond parameter, C—O vs O—H and C—O—H vs O—H, have been investigated for hydrogen-bonded carboxyl groups using accurate neutron diffraction data. The C—O length decreases linearly with increasing O—H length, but the C—O—H angle does not show correlation and scatters over several degrees.

Introduction

Correlations between hydrogen-bond parameters, such as O—H vs O...O distances, were first pointed out by Nakamoto, Margoshes & Rundle (1955) (see Hamilton & Ibers, 1968; Olovsson & Jönsson, 1976; Ichikawa, 1978). The effect of the strength of hydrogen bonding on the bonding parameters is not confined to the hydrogen-bond system, OHO, but extends to the neighbouring atomic groups. It seems useful to establish first the correlation between the bonding parameters affected by hydrogen

bonding by means of an empirical relationship. In another paper (Ichikawa, 1979) the effect of distortion of a carboxyl group (COOH) due to hydrogen bonding has been investigated systematically from accurately determined X-ray crystal-structure data; the variations of the bond lengths and angles in the carboxyl group were studied as a function of the hydrogen-bond length O...O. However, an examination of the direct correlation at the hydrogen-bond donor O atom, *i.e.* the correlation between C—O and O—H lengths and between the C—O—H angle and the O—H length (C is the carbon atom bonded to the hydrogen-bond donor O atom), was precluded because of inaccuracy of the H-atom position from the X-ray data.

The aim of this paper is to discuss the C—O vs O—H and C—O—H vs O—H correlations in compounds which include carboxyl groups (COOH) with neutron-diffraction data. The carboxyl group is used as an example for the following reasons: (i) This is one of the structural groups occurring most commonly in crystals and many suitable examples can be found. (ii) Many molecular crystals containing this group exhibit short hydrogen bonds, a condition where the most significant O—H length dependence can be expected. This

Table 1. O—H and C—O lengths, and C—O—H angles in hydrogen-bonded carboxyl groups together with O...O distances

Numbers in parentheses are the standard deviations in the least significant digit.

Compound	Reference	O...O (Å)	O—H (Å)	C—O (Å)	C—O—H (°)
Ammonium tetroxalate	1	2.520 (5)	1.040 (7)	1.291 (4)	112.9 (3)
		2.500 (4)	1.102 (7)	1.288 (4)	113.4 (3)
		2.472 (4)	1.069 (7)	1.296 (4)	112.5 (3)
Potassium hydrogen oxydiacetate	2	2.476 (2)	1.152 (3)	1.294 (2)	111.5 (2)
Glycolic acid	3	2.647 (2)	1.003 (2)	1.314 (1)	109.4 (2)
		2.638 (2)	1.001 (2)	1.310 (1)	110.9 (2)
α -(COOH) ₂ .2H ₂ O	4	2.506 (4)	1.026 (7)	1.291 (5)	114.4 (6)
Dipeptide glycylglycine.HCl.H ₂ O	5	2.644 (5)	1.003 (7)	1.316 (4)	111.7 (4)
N-Acetylglycine	6	2.562 (5)	1.034 (8)	1.308 (4)	111.7 (4)
Ammonium glycinium sulphate	7	2.598 (3)	1.022 (5)	1.308 (3)	113.1 (3)
Potassium hydrogen chloromaleate	8	2.403 (3)	1.206 (5)	1.277 (3)	113.6 (3)
		—	1.199 (5)	1.280 (3)	111.1 (3)

References: (1) Currie, Speakman & Curry (1967); (2) Albertsson & Grenthe (1973); (3) Ellison, Johnson & Levy (1971); (4) Sabine, Cox & Craven (1969); (5) Koetzle, Hamilton & Parthasarathy (1972); (6) Mackay (1975); (7) Vilminot & Philippot (1976); (8) Ellison & Levy (1965).

study is part of a systematic evaluation of the distortion of structural groups due to hydrogen bonding.

Crystal-structure data used in the study are taken from neutron diffraction analyses in the literature and part of the data was retrieved with the *TOOL-IR* system (Yamamoto, Negishi, Ushimaru, Tozawa, Okabe & Fujiwara, 1975). The relevant parameters were recalculated with *UNICS* (1967) if they and their estimated standard deviations were not specified. Values uncorrected for thermal motion were used. Data were included in this study only if the e.s.d.'s of all the relevant lengths were equal to or less than 0.010 Å and the O...O hydrogen-bond length was less than 2.7 Å. Carboxyl groups connected by a symmetric hydrogen bond were excluded from the data because the 'structure' and nature of the symmetric hydrogen bond are still not completely understood (Catti & Ferraris, 1976; Olovsson & Jönsson, 1976; Ichikawa, 1978).

Results and discussion

The relevant parameters are given in Table 1. As shown in Fig. 1, there is a correlation between the C—O and O—H lengths: C—O decreases linearly with increasing O—H (*i.e.* decreasing O...O), both being in a competitive relationship. It can be estimated from Fig. 1 that the C—O length shortens by about 0.035 Å when the O—H length increases from its nonhydrogen-bonded value of 0.96 Å to about 1.20 Å when

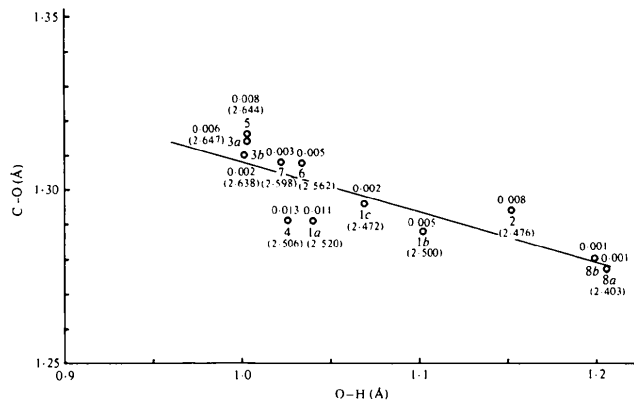


Fig. 1. Diagram of the correlation between C—O and O—H distances in hydrogen-bonded carboxyl groups. The straight line is the least-squares fit of data points. The number of compounds and the deviations of each point from the line are given together with the O...O distances in parentheses.

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Crystal and molecular structure of a sympathomimetic amine, tyramine hydrochloride. BY ALOKA PODDER, J. K. DATTA GUPTA and N. N. SAHA, *Crystallography and Molecular Biology Division, Saha Institute of Nuclear Physics, Calcutta 700009, India* and W. SAENGER, *Max-Planck-Institut für Experimentelle Medizin, Abteilung Chemie, D-3400 Göttingen, Federal Republic of Germany*

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Abstract

A printer's error is corrected. In Table 1 of the paper by Podder, Dattagupta, Saha & Saenger [*Acta Cryst.* (1979), **B35**, 649–652] the value for *b* should be 10.768 (2) Å.

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forming a strong hydrogen bond. On the other hand, no correlation could be found between C—O—H angle and O—H length: the C—O—H angles are randomly distributed over 109.4 ~ 114.4° with a mean value of 112.2° (Table 1).

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All the relevant information is contained in the *Abstract*.

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