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The Crystal Structure of 3,4,5-Trimethylbenzoic Acid

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Crystals of 3,4,5-trimethylbenzoic acid have been studied by three-dimensional Fourier methods. They are monoclinic, space group $P2_1/c$, with four molecules per unit cell. The lattice constants are $a=7{\cdot}69_8$, $b=10{\cdot}20_3$, $c=12{\cdot}01_3$ Å and $\beta=108°40'$. The crystal structure was solved by Patterson syntheses, and was refined by three-dimensional Fourier and differential syntheses and least-squares methods. The final R index, for 1300 independent reflexions, was 0·091. The structure consists of dimers linked together by hydrogen bonds. The carboxyl group is twisted 5·1 ° with respect to the plane of the benzene ring. Bond lengths and bond angles are normal.

Introduction

The molecular structures of derivatives of benzoic acid have been studied by several authors: Ossorio (1960) has studied the ultraviolet absorption spectra of benzoic acid, toluic acid and dimethylbenzoic acid, and has interpreted such spectra in relation to the theory of resonance and of steric hindrance; Sim, Robertson & Goodwin (1955) have determined the crystal structure of benzoic acid; Ferguson & Sim (1961, 1962) have discussed molecular overcrowding in *o*-chlorobenzoic acid and *o*-bromobenzoic acid, two isomorphous compounds; Brown & Marsh (1963) have obtained the structure of 2-amino-3-methylbenzoic acid; Anca, Martinez-Carrera & García-Blanco (1967) have given the structure of 2,6-dimethylbenzoic acid, Martinez, Martinez-Carrera & García-Blanco (1967) have studied 3,5-dimethylbenzoic acid, and Florencio & Smith (1968) have studied 2,4,6-trimethylbenzoic acid. Such studies demonstrate that when the methyl groups are close to the carboxyl group there are interactions between them which result in a twisting of the carboxyl group with respect to the benzene ring. No such distortion occurs in 3,4,5-trimethylbenzoic acid, the structure of which is reported here.

Crystal data

A purified specimen of 3,4,5-trimethylbenzoic acid was kindly supplied by Dr Colomina, of our Institute. Single crystals were obtained by slow evaporation in ethyl alcohol. The crystals were needle-shaped prisms

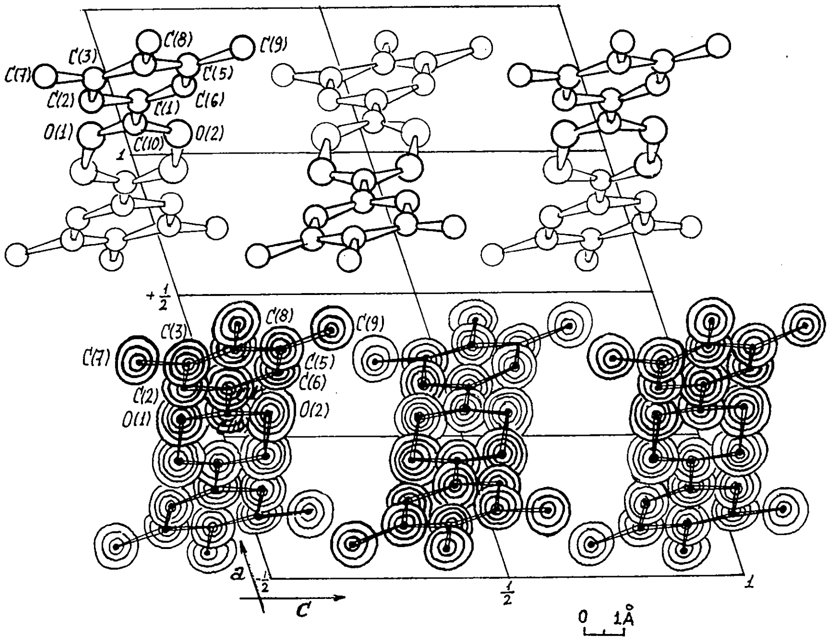

Fig. 1. A composite diagram of the last electron density function.

extending along the *b* axis, and belonging to the monoclinic system.

Cell dimensions were measured from Weissenberg photographs of the three zero levels, upon which Debye–Scherrer diagrams with aluminum powder as standard were superimposed. The crystal data values obtained were: $a=7{\cdot}69_8$, $b=10{\cdot}20_3$, $c=12{\cdot}01_3$ Å, $\beta=108°4_0'$, $D_m=1{\cdot}1_7$, $D_x=1{\cdot}19_4$ g.cm^{-3}, $Z=4$.

Systematic absences were consistent with the space group $P2_1/c$, but a few weak reflexions *h*0*l* with *l* odd appeared in a photograph taken along [010], but none were observed in photographs taken along [001]. The fact that their shape was different from those of normal reflexions, and also the absence of the $K\beta$ component when unfiltered radiation was used, led to the conclusion that such reflexions were Renninger reflexions. This was later confirmed by the geometry of the reciprocal lattice.

Experimental

Intensity data were obtained with Cu $K\alpha$ radiation from multiple-film integrated Weissenberg photographs of seven layers along [100] and five along [010]. A total of 1300 independent reflexions were measured

Table 1. *Final atomic parameters*

Estimated standard deviations in parentheses.

(*a*) Fractional coordinates

	x/a	y/b	z/c
C(1)	0·1691 (5)	0·3101 (4)	0·0472 (3)
C(2)	0·1788 (5)	0·3875 (4)	−0·0469 (3)
C(3)	0·2468 (5)	0·5150 (4)	−0·0282 (3)
C(4)	0·3062 (5)	0·5649 (4)	0·0856 (4)
C(5)	0·2978 (5)	0·4878 (4)	0·1812 (4)
C(6)	0·2286 (5)	0·3611 (4)	0·1611 (4)
C(7)	0·2552 (7)	0·5943 (5)	−0·1337 (4)
C(8)	0·3812 (7)	0·7042 (4)	0·1081 (5)
C(9)	0·3653 (8)	0·5370 (5)	0·3068 (4)
C(10)	0·0963 (5)	0·1757 (4)	0·0279 (3)
O(1)	0·0571 (5)	0·1292 (3)	−0·0769 (3)
O(2)	0·0731 (5)	0·1111 (3)	0·1105 (3)

(*b*) Anisotropic temperature coefficients*

	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{13}
C(1)	0·0124 (6)	0·0060 (3)	0·0064 (3)	−0·0010 (3)	0·0000 (4)	0·0028 (4)
C(2)	0·0148 (8)	0·0066 (4)	0·0068 (3)	−0·0010 (3)	−0·0044 (3)	0·0032 (4)
C(3)	0·0129 (7)	0·0064 (4)	0·0075 (3)	0·0010 (3)	0·0004 (2)	0·0036 (4)
C(4)	0·0135 (8)	0·0060 (4)	0·0086 (4)	0·0008 (4)	−0·0008 (3)	0·0038 (4)
C(5)	0·0141 (8)	0·0066 (4)	0·0071 (3)	0·0003 (3)	−0·0010 (3)	0·0030 (4)
C(6)	0·0133 (7)	0·0071 (4)	0·0070 (3)	0·0003 (3)	−0·0005 (3)	0·0028 (4)
C(7)	0·0243 (9)	0·0098 (5)	0·0081 (4)	−0·0018 (6)	0·0023 (3)	0·0055 (5)
C(8)	0·0273 (9)	0·0063 (4)	0·0131 (5)	−0·0038 (5)	−0·0019 (4)	0·0077 (7)
C(9)	0·0317 (9)	0·0113 (6)	0·0077 (4)	−0·0032 (7)	−0·0033 (4)	0·0045 (6)
C(10)	0·0165 (8)	0·0061 (3)	0·0069 (3)	−0·0010 (3)	0·0000 (4)	0·0041 (3)
O(1)	0·0307 (9)	0·0081 (3)	0·0076 (3)	−0·0045 (4)	−0·0019 (3)	0·0052 (4)
O(2)	0·0325 (8)	0·0081 (3)	0·0077 (2)	−0·0058 (4)	0·0001 (2)	0·0050 (3)

* In the expresion $f=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\dots+2\beta_{23}kl)]$.

Table 2. *Bond lengths and valence angles*

C(1)—C(2)	1·400 (5) Å	C(1)-C(2)—C(3)	120·7 (3)°
C(2)—C(3)	1·394 (5)	C(2)-C(3)—C(4)	119·2 (3)
C(3)—C(4)	1·391 (5)	C(3)-C(4)—C(5)	120·6 (3)
C(4)—C(5)	1·410 (5)	C(4)-C(5)—C(6)	119·6 (3)
C(5)—C(6)	1·400 (5)	C(5)-C(6)—C(1)	120·2 (3)
C(6)—C(1)	1·397 (5)	C(6)-C(1)—C(2)	119·7 (3)
C(7)—C(3)	1·523 (6)	C(2)-C(3)—C(7)	118·4 (3)
		C(7)-C(3)—C(4)	122·4 (3)
C(8)—C(4)	1·526 (6)	C(3)-C(4)—C(8)	120·1 (4)
		C(8)-C(4)—C(5)	119·3 (4)
C(9)—C(5)	1·516 (7)	C(4)-C(5)—C(9)	122·4 (4)
		C(9)-C(5)—C(6)	118·1 (4)
C(1)—C(10)	1·472 (5)	C(6)-C(1)—C(10)	119·3 (3)
		C(2)-C(1)—C(10)	121·0 (3)
C(10)-O(1)	1·287 (5)	C(1)-C(10)-O(1)	117·2 (3)
C(10)-O(2)	1·251 (5)	C(1)-C(10)-O(2)	120·1 (3)
		O(1)-C(10)-O(2)	122·1 (3)

by means of a Nonius microdensitometer. Non-observed reflexions were given values of half the intensity of the weakest observed spot on the same layer. No absorption correction was necessary. The data were reduced to structure amplitudes in the usual way, and were scaled according to the method of Rollett & Sparks (1960). A comparison was made of observed F values, which were common to two different crystal settings. The ratios of these common values did not differ by more than 6%; therefore the values of all observed reflexions were included in the calculations.

Determination of the structure

$P(v,w)$ and $P(u,w)$ Patterson functions were calculated for the 105 $0kl$ and the 76 $h0l$ observed independent reflexions. A sharpening factor

$$\frac{1}{f^2}\exp\left[2B\left(\frac{\sin\theta}{\lambda}\right)^2\right]\cdot\left(2\frac{\sin\theta}{\lambda}\right)^4 \exp\left[-\left(4{\cdot}4\frac{\sin\theta}{\lambda}\right)^2\right]$$

(see Donohue & Trueblood, 1952; Brown & Marsh, 1963) was used. A preliminary isotropic temperature factor $B=2{\cdot}87$ was obtained from a Wilson plot. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Both projections showed clearly a symmetric distribution of the maxima corresponding to the intramolecular vectors around the origin. From these the twist in orientation and height of the molecule was quite apparent and, despite a certain degree of overlapping, the coordinates of all carbon atoms and the two oxygen atoms could be obtained, giving for the approximate structure an R_{0kl} index of 0·28 and an R_{h0l} index of 0·29 for the reflexions used.

Three-dimensional refinement

For the 1300 reflexions used the approximate coordinates found as above lead to an R index of 0·38. Atomic parameters were then refined by three consecutive three-dimensional Fourier syntheses. In the first synthesis only reflexions with $\sin\theta$ less than 0·7 were included, the R value dropping to 0·20. Fig. 1 shows the electron density map from the last synthesis, together with a schemetic view of the structure.

Next, four cycles of differential synthesis were carried out using individual isotropic temperature factors, and an other four cycles with anisotropic temperature factors. These syntheses were stopped when the shifts in the parameters were less than three times the value of the standard deviation. The new agreement index was $R=0{\cdot}12$.

The refinement proceeded by three cycles of least-squares synthesis. A full-matrix program written by Busing, Martin & Levy (1962) was used, in which the weighting scheme was that of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961): $w_{hkl}=(a+|F_o|+c|F_o|^2)^{-1/2}$ with $a=2|F_o|_{\min}$ and $c=2/|F_o|_{\max}$. The R value achieved was 0·11. Together with the above calculations inter- and intramolecular distances and bond angles were obtained as a test of the improvement in the structure.

Finally a difference synthesis gave positions for the hydrogen atoms which were consistent with the coordinates of the binding carbon and oxygen atoms. They

Table 3. *Intermolecular distances less than* 4 Å

The following roman numbers give the symmetry relationship of the atoms concerned

I	(x	y	z)	VII	(x	$\frac{2}{3}-y$	$-\frac{1}{2}+z$)
II	($-x$	$1-y$	$-z$)	VIII	($-x$	$\frac{1}{2}+y$	$-\frac{1}{2}-z$)
III	($1-x$	$1-y$	$-z$)	IX	($1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$)
IV	(x	$\frac{1}{2}-y$	$-\frac{1}{2}+z$)	X	($-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$)
V	($1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$)	XI	($-x$	$-y$	$-z$)
VI	(x	$\frac{1}{2}-y$	$\frac{1}{2}+z$)				

Atom i	Atom j	$d(ij)$	Atom i	Atom j	$d(ij)$
C(1)(I)	C(3)(II)	3·608	C(6)(I)	C(7)(II)	3·661
C(1)(I)	C(4)(II)	3·717	C(6)(I)	O(1)(VI)	3·789
C(1)(I)	C(7)(II)	3·858	C(6)(I)	C(8)(V)	3·732
C(2)(I)	C(3)(II)	3·799	C(7)(I)	C(9)(VII)	3·970
C(2)(I)	C(4)(II)	3·644	C(7)(I)	O(1)(VIII)	3·551
C(2)(I)	C(5)(II)	3·727	C(7)(I)	O(2)(II)	3·994
C(2)(I)	C(6)(II)	3·942	C(7)(I)	O(2)(IV)	3·610
C(2)(I)	C(8)(III)	3·806	C(8)(I)	C(9)(IX)	3·886
C(2)(I)	O(2)(IV)	3·930	C(8)(I)	C(10)(II)	3·719
C(3)(I)	C(3)(III)	3·749	C(8)(I)	O(1)(II)	3·680
C(3)(I)	C(4)(III)	3·808	C(9)(I)	O(1)(VI)	3·553
C(3)(I)	C(6)(II)	3·714	C(9)(I)	O(2)(X)	3·884
C(3)(I)	C(7)(III)	3·866	C(10)(I)	C(10)(XI)	3·856
C(3)(I)	C(8)(III)	3·987	C(10)(I)	O(1)(XI)	3·442
C(4)(I)	C(7)(III)	3·622	C(10)(I)	O(2)(XI)	3·411
C(4)(I)	C(10)(II)	3·969	O(1)(I)	O(1)(XI)	3·484
C(5)(I)	C(7)(III)	3·758	O(2)(I)	O(2)(XI)	3·397
	(Hydrogen bond)		O(1)(I)	O(2)(XI)	2·628

were included in a final cycle of least squares, where the temperature factors of the hydrogen atoms were made equal to those of the corresponding binding atoms, but were not allowed to vary. The final R index was 0·091.

Final parameters

Final atomic parameters and standard deviations are given in Table 1. Bond lengths and angles are shown in Table 2; the mean standard deviations are 0·005 Å and 0·3° respectively. Intermolecular distances less than 4 Å are shown in Table 3. Equations of all the mean-square planes through (*a*) all atoms, (*b*) through atoms in the aromatic ring, and (*c*) through atoms in the carboxyl group and C(1), have been calculated (Schomaker, Waser, Marsh & Bergman, 1959):

(*a*) All atoms:

$$0{\cdot}9278X' - 0{\cdot}3496Y + 0{\cdot}1304Z' - 0{\cdot}0007 = 0$$

(*b*) Ring:

$$0{\cdot}9303X' - 0{\cdot}3457Y + 0{\cdot}1230Z' - 0{\cdot}0141 = 0$$

(*c*) Carboxyl group and C(1):

$$0{\cdot}9064X' - 0{\cdot}3608Y + 0{\cdot}2197Z' - 0{\cdot}0070 = 0$$

Here X', Y and Z' (in Å) are referred to the orthogonal axes a, b and c'. Deviations of atoms from the mean-square planes are given in Table 4. It may be concluded that the molecule is fairly planar, the angle between the plane of the aromatic ring and the plane of the carboxyl group being 5·1°. A comparison between observed and calculated structure factors is given in Table 5. Table 6 gives the hydrogen atom coordinates.

Discussion of the structure

There is no deviation from hexagonal symmetry for the bond lengths and angles in the aromatic ring (Table 2), the average value for the C–C distance in the ring being 1·398 Å in agreement with the value of 1·395 Å usually reported in the literature (Pauling, 1960). The bond lengths corresponding to C(3)–C(7), C(4)–C(8), C(5)–C(9) and C(1)–C(10) are also normal. The values found for the C(10)–O(1) bond length and for the C(1)–C(10)–O(1) bond angle clearly indicate that the hydrogen atom is attached to the O(1) atom. The mean C–H bond distance is 0·986 Å and the mean C–C–H angle 109°, in the methyl groups.

Table 4. *Displacements of the atoms from the various planes*

(i) Plane through all atoms
(ii) Plane through benzene ring atoms
(iii) Plane through carboxyl group and C(1)

	(i)	(ii)	(iii)
C(1)	0·003 Å	0·000 Å	−0·001 Å
C(2)	−0·008	0·002	−0·125
C(3)	−0·016	−0·002	−0·139
C(4)	−0·007	−0·001	−0·020
C(5)	0·008	0·003	0·110
C(6)	0·007	−0·003	0·113
C(7)	−0·018	0·009	−0·267
C(8)	−0·016	−0·005	−0·033
C(9)	0·052	0·038	0·275
C(10)	0·002	−0·005	0·004
O(1)	0·099	0·099	−0·001
O(2)	−0·106	−0·124	−0·002

The molecule is basically planar. It can be seen from Table 4 that C(7) and C(9) are above, and C(8) is below, the mean-square plane. This indicates a degree of molecular overcrowding. The rotation of the carboxyl group around the C(1)–C(10) bond is small, being only 5·1° away from the plane of the ring. The values for 2,6-dimethylbenzoic, 2,4,6-trimethylbenzoic, *o*-bromobenzoic, *o*-chlorobenzoic and *o*-fluorobenzoic

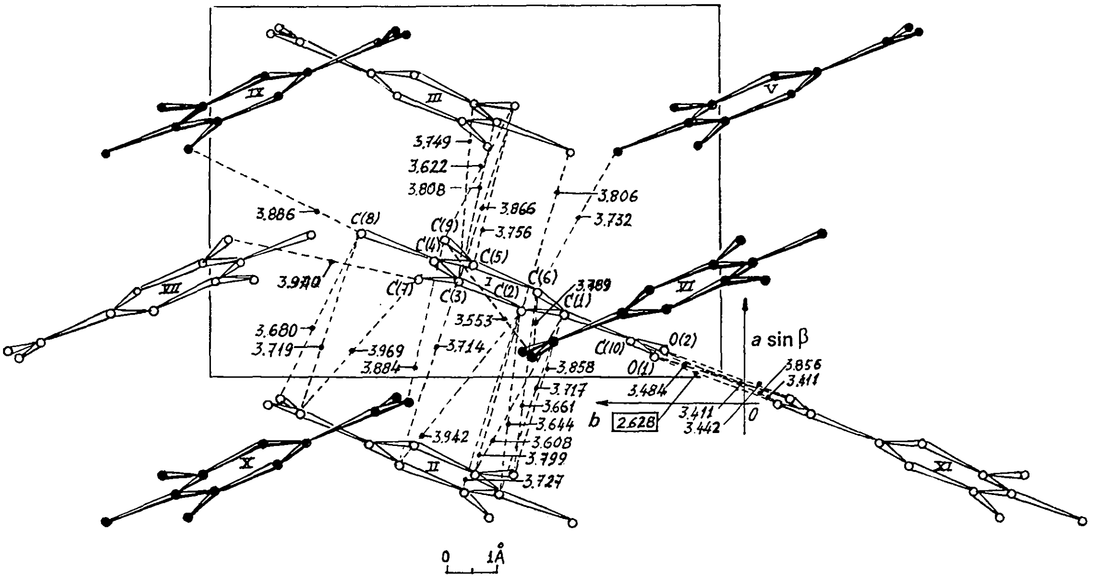

Fig. 2. Intermolecular distances less than 4 Å.

Table 5. *Observed and calculated structure factors*

H	K	L	FOBS	FCAL
		2	83.8	80.7
		4	43.2	44.0-
		6	4.0	4.1-
		8	12.5	13.2-
		10	2.2	.8-
		12	3.6	3.6-
	1	1	38.7	41.5-
	1	2	13.3	11.4-
	1	3	.0	.1*
	1	4	24.1	24.8
	1	5	12.7	11.6-
	1	6	3.0	1.0-
	1	7	11.0	10.4-
	1	8	15.8	16.5-
	1	9	10.8	10.7
	1	10	9.2	9.2-
	1	11	5.1	4.0
	1	12	1.0	2.3-*
	1	13	1.7	.6*
	1	14	1.3	.51*
	2		34.1	32.9
	2	1	2.6	3.5
	2	2	24.0	23.3-
	2	3	10.3	9.0-
	2	4	3.4	2.6-
	2	5	11.2	11.5-
	2	6	12.3	12.0
	2	7	7.0	7.5
	2	8	7.5	7.0-
	2	9	1.7	.51*
	2	10	5.6	5.7
	2	11	11.5	11.4-
	2	12	1.5	1.61*
	3	1	16.0	15.0-
	3	2	20.8	20.3-
	3	3	25.4	22.9-
	3	4	42.9	41.2
	3	5	1.3	.2-*
	3	6	23.9	22.2
	3	7	4.2	3.9
	3	8	1.6	.2-*
	3	9	4.3	5.5-
	3	10	4.2	7.3-
	3	11	4.2	4.2-
	3	12	4.5	4.7-
	3	13	1.2	.3-*
	4		37.5	37.9-
	4	1	10.7	10.2-
	4	2	21.4	19.4-
	4	3	6.3	3.8-
	4	4	28.3	27.2
	4	5	11.3	9.0-
	4	6	17.7	16.4
	4	7	1.6	.4-*
	4	8	4.5	4.9-
	4	9	9.5	10.1
	4	10	5.0	4.0
	4	11	3.9	4.1
	4	12	1.6	.31*
	4	13	2.1	1.4
	5	1	23.3	20.9-
	5	2	5.0	6.9
	5	3	4.7	4.1
	5	4	5.5	5.1
	5	5	9.4	8.7
	5	6	9.8	9.1-
	5	7	7.8	7.1
	5	8	4.9	3.4
	5	9	3.8	2.1-
	5	10	1.8	1.91*
	5	11	3.4	3.4-
	5	12	1.4	.3-*
	5	13	1.0	2.2
	6		14.8	12.5
	6	1	11.5	10.9-
	6	2	5.6	4.5
	6	3	5.3	4.4-
	6	4	15.2	14.6
	6	5	7.5	9.0
	6	6	12.8	14.2
	6	7	5.5	5.0
	6	8	5.4	5.5-
	6	9	9.3	8.1
	6	10	1.7	1.9-*
	6	11	3.2	3.5
	7	1	11.3	10.9
	7	2	1.7	.7-*
	7	3	3.2	3.6
	7	4	8.8	8.8-
	7	5	19.3	20.6-
	7	6	29.6	29.7-
	7	7	9.4	7.7-
	7	8	10.2	10.5-
	7	9	4.2	4.3
	8		10.3	9.4
	8	1	7.0	7.0
	8	2	1.8	2.2-*
	8	3	9.4	9.3
	8	4	4.2	5.0-
	8	5	1.9	1.21*
	8	6	3.5	3.3
	8	7	1.8	1.2-*
	8	8	2.6	2.4-
	9	1	4.1	4.4-
	9	2	3.1	3.7-
	9	3	3.7	2.5-
	9	4	11.5	10.7
	9	5	12.0	11.5-
	9	6	1.9	1.31*
	9	7	2.7	2.8-
	9	8	1.5	.1*
	9	9	2.2	2.3
	9	10	2.0	2.7
	10		10.0	11.7
	10	1	1.8	2.81*
	10	2	6.8	6.8
	10	3	1.8	2.01*
	10	4	1.7	1.4-*
	10	5	2.5	2.7
	10	6	1.6	.1-*
	10	7	2.0	3.0
	11	1	6.7	3.9-
	11	2	4.4	3.9-
	11	3	1.6	.91*
	11	4	1.8	1.71*
	11	5	1.6	.81*
	11	6	1.2	.61*
	11	7	3.2	2.4
	12		3.0	4.1-
	12	1	1.9	.1-*
	12	2	1.7	.3-*
	12	3	1.2	.8*
	12	4	3.0	3.6
	12	5	2.7	3.1
-1		14	2.7	2.6
-1		12	1.8	.91*
-1		10	13.2	12.9-
-1		8	3.6	3.4-
-1		6	27.1	25.5-
-1		4	3.1	2.1
-1		2	92.9	95.2
1			30.6	65.1
1		2	38.1	30.2
1		4	2.3	1.4-
1		6	7.6	8.5-
1		8	3.7	3.6
1		10	2.9	2.8
1		12	3.6	2.4-
1		14	3.3	3.7-
-1	1	14	3.4	2.7-
-1	1	13	3.6	1.5-*
-1	1	12	4.2	6.5-
-1	1	11	12.7	11.2
-1	1	10	18.1	17.0-
-1	1	9	26.0	27.2
-1	1	8	13.3	12.9-
-1	1	7	10.1	8.3-
-1	1	6	12.7	9.8
-1	1	5	18.1	17.7-
-1	1	4	12.7	11.6
-1	1	3	20.3	20.2
-1	1	2	1.5	1.7
-1	1	1	4.0	3.2
1	1		27.1	25.7-
1	1	1	41.0	42.7
1	1	2	38.7	40.5-
1	1	3	15.6	15.0-
1	1	4	20.1	19.3-
1	1	5	25.6	24.2-
1	1	6	2.8	1.5
1	1	7	1.4	.81*
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1	3	5	1.0	1.21*
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1	3	7	1.2	1.61*
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1	3	10	1.4	1.2-*
1	3	11	1.5	.11*
1	3	12	1.3	2.4-*
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1	4	7	6.1	5.1
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1	4	9	2.6	2.1
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1	4	11	2.8	3.6
1	4	12	1.4	1.61*
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1	5	7	3.0	3.8
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1	6	2	1.5	.6
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1	6	7	6.8	7.2-
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1	8	5	3.6	4.5-
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1	9	3	10.2	13.3-
1	9	4	10.2	16.2
1	9	5	5.6	9.1-
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1	10	1	1.1	2.51*
1	10	2	1.1	2.31*
1	10	3	3.0	4.9-
1	10	4	1.0	3.91*
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2	1	12	1.1	.11*
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-2	2	13	1.3	1.0-
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-2	2	11	1.2	.91*
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2	2	7	1.1	1.5-*
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2	10	4	6.0	5.7-
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2	10	6	.6	.91*
2	10	7	3.2	3.0
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2	11		6.0	5.7-
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-2	12	1	3.1	2.4-
2	12		1.1	2.6-
2	12	1	3.0	4.3-
2	12	2	1.0	2.0-
2	12	3	1.5	1.7-

Table 5 (*cont.*)

H	K	L	FOBS	FCAL
2	12	4	2.4	2.5-
-3		14	1.0	.4-*
-3		12	11.3	14.3
-3		10	38.2	43.0
-3		8	6.4	7.4
-3		6	20.2	20.0-
-3		4	1.1	1.3-*
-3		2	14.4	14.0-
3			13.8	14.5
3		2	21.1	22.0-
3		4	31.4	31.3-
3		6	1.8	.3
3		8	5.1	5.0-
3		10	3.4	3.5-
-3	1	15	.6	.7-*
-3	1	14	3.3	1.6
-3	1	13	1.0	1.9
-3	1	12	3.5	2.8-
-3	1	11	7.0	6.2-
-3	1	10	1.6	.11*
-3	1	9	8.2	8.1-
-3	1	8	4.4	3.6
-3	1	7	10.1	9.7-
-3	1	6	8.4	7.9-
-3	1	5	10.1	9.0-
-3	1	4	12.7	11.5
-3	1	3	2.8	2.5
-3	1	2	36.9	41.0
-3	1	1	15.0	15.7
3	1		18.3	17.6-
3	1	1	5.6	6.2
3	1	2	3.4	3.8-
3	1	3	9.3	7.9
3	1	4	10.8	8.6
3	1	5	13.3	10.9
3	1	6	7.0	7.1
3	1	7	1.6	.51*
3	1	8	1.7	1.6-*
3	1	9	1.6	.2-*
3	1	10	3.1	2.8-
3	1	11	2.6	2.5-
3	1	12	1.1	.61*
-3	2	15	4.7	3.6-
-3	2	14	.9	.9-*
-3	2	13	1.2	1.2-*
-3	2	12	3.2	2.9-
-3	2	11	2.1	2.3
-3	2	10	6.8	5.8
-3	2	9	1.3	.81*
-3	2	8	5.2	5.7-
-3	2	7	1.1	.8-*
-3	2	6	3.6	3.1
-3	2	5	7.0	2.1-
-3	2	4	9.6	9.3
-3	2	3	.7	.2-*
-3	2	2	11.7	9.9-
-3	2	1	24.0	26.0
3	2		25.7	25.8
3	2	1	34.2	35.1-
3	2	2	2.9	3.3
3	2	3	3.5	3.1
3	2	4	4.3	4.1-
3	2	5	10.1	10.3
3	2	6	5.8	6.0
3	2	7	4.2	3.6
3	2	8	9.4	9.6-
3	2	9	4.3	3.2
3	2	10	3.2	3.0-
3	2	11	1.2	1.2-*
-3	3	15	.5	.3*
-3	3	14	5.1	5.2
-3	3	13	3.3	3.2-
-3	3	12	2.2	2.0-
-3	3	11	5.5	4.9-
-3	3	10	1.4	1.1-*
-3	3	9	4.6	4.1-
-3	3	8	2.2	2.5
-3	3	7	7.0	7.8-
-3	3	6	27.6	25.3-
-3	3	5	1.0	1.51*
-3	3	4	22.5	21.5-
-3	3	3	2.7	2.2
-3	3	2	8.6	7.6
-3	3	1	27.2	25.8-
3	3		29.1	29.5-
3	3	1	16.3	14.3-
3	3	2	15.3	13.7-
3	3	3	1.1	2.0-*
3	3	4	14.7	14.6
3	3	5	3.5	3.0
3	3	6	4.0	3.2
3	3	7	12.2	12.0
3	3	8	8.7	7.9-
3	3	9	13.4	13.0
3	3	10	5.2	4.3-
3	3	11	3.2	3.0
3	3	12	.7	[illegible]
-3	4	14	2.1	1.7
-3	4	13	2.2	2.0-
-3	4	12	5.4	4.9-
-3	4	11	1.5	.71*
-3	4	10	8.6	7.9-
-3	4	9	5.6	6.6
-3	4	8	1.4	2.8-*
-3	4	7	3.3	2.3
-3	4	6	21.7	20.6
-3	4	5	1.1	.4-*
-3	4	4	13.6	11.9
-3	4	3	5.4	5.4
-3	4	2	7.8	7.3-
-3	4	1	21.0	21.3-
3	4		16.3	15.1
3	4	1	21.2	21.6
3	4	2	2.7	2.3-
3	4	3	5.2	4.3
3	4	4	5.9	5.6-
3	4	5	3.2	3.1
3	4	6	2.9	2.4
3	4	7	5.0	5.7
3	4	8	6.7	6.8-
3	4	9	4.8	4.2
3	4	10	1.2	.61*
3	4	11	1.1	1.1-*
-3	5	14	1.1	1.6
-3	5	13	2.3	2.2-
-3	5	12	1.9	1.5
-3	5	11	6.2	6.0-
-3	5	10	3.7	3.4-
-3	5	9	1.2	.71*
-3	5	8	1.2	1.6-*
-3	5	7	7.6	7.0
-3	5	6	1.1	.2-*
-3	5	5	2.9	3.1
-3	5	4	7.2	7.4
-3	5	3	1.9	1.2-
-3	5	2	5.5	4.5-
-3	5	1	7.1	6.6-
3	5		3.3	4.2
3	5	1	1.5	1.3-
3	5	2	1.0	1.41*
3	5	3	8.0	7.7
3	5	4	9.9	8.4
3	5	5	3.6	2.7-
3	5	6	8.4	8.4-
3	5	7	5.4	4.6-
3	5	8	4.0	3.7-
3	5	9	1.3	.11*
3	5	10	.9	1.91*
-3	6	13	.7	.3*
-3	6	12	3.3	2.8
-3	6	11	2.7	2.7-
-3	6	10	6.5	6.2
-3	6	9	6.1	5.1
-3	6	8	1.2	1.81*
-3	6	7	2.5	1.4
-3	6	6	15.6	15.7
-3	6	5	10.7	10.0-
-3	6	4	13.5	12.9
-3	6	3	12.4	10.6-
-3	6	2	16.2	15.4-
-3	6	1	21.2	20.3-
3	6		3.8	3.0-
3	6	1	6.5	5.7
3	6	2	2.0	1.9
3	6	3	14.4	13.4-
3	6	4	11.2	11.1-
3	6	5	12.7	11.8-
3	6	6	6.2	4.7-
3	6	7	4.0	4.5-
3	6	8	3.0	2.9-
3	6	9	1.0	.5-*
3	6	10	.7	2.2-*
-3	7	13	1.4	1.8
-3	7	12	.8	1.2-*
-3	7	11	1.0	1.31*
-3	7	10	1.1	.2-*
-3	7	9	5.0	4.7
-3	7	8	3.0	2.9
-3	7	7	1.2	.9-*
-3	7	6	11.6	9.9
-3	7	5	24.6	25.5-
-3	7	4	29.0	30.3
-3	7	3	4.8	6.2-
-3	7	2	14.0	12.7
-3	7	1	14.0	15.0
3	7		8.4	7.8
3	7	1	2.7	2.1
3	7	2	2.7	2.7-
3	7	3	2.7	2.3
3	7	4	1.2	.2-*
3	7	5	2.3	1.9
3	7	6	1.2	1.4-*
3	7	7	1.6	1.4-
3	7	8	3.4	3.0
3	7	9	.9	.31*
-3	8	12	.5	.91*
-3	8	11	.8	.7-*
-3	8	10	3.7	2.9
-3	8	9	5.2	4.6-
-3	8	8	6.0	5.4-
-3	8	7	1.2	.41*
-3	8	6	1.2	.71*
-3	8	5	3.1	3.1
-3	8	4	6.3	4.6
-3	8	3	2.0	1.3-
-3	8	2	4.4	3.0-
-3	8	1	2.5	1.7-
3	8		1.2	.81*
3	8	1	1.3	1.91*
3	8	2	4.3	3.9
3	8	3	5.6	5.3
3	8	4	2.6	1.6-
3	8	5	1.2	1.3-*
3	8	6	2.7	2.3
3	8	7	4.5	4.2-
3	8	8	1.9	1.0
3	8	9	.6	1.01*
-3	9	11	.5	1.8-*
-3	9	10	1.8	1.6
-3	9	9	4.5	2.9-
-3	9	8	1.0	1.1
-3	9	7	5.8	5.1-
-3	9	6	11.2	10.8-
-3	9	5	12.3	11.0-
-3	9	4	1.2	.2-*
-3	9	3	1.2	.8-*
-3	9	2	1.2	.71*
-3	9	1	3.0	3.9
3	9		2.7	2.5
3	9	1	4.2	4.2
3	9	2	10.8	10.0-
3	9	3	11.0	10.5
3	9	4	4.6	3.5-
3	9	5	4.3	3.1
3	9	6	2.6	1.9
3	9	7	.8	1.51*
3	9	8	.5	1.4-*
-3	10	10	.6	4.11*
-3	10	9	3.5	3.0-
-3	10	8	2.0	2.3
-3	10	7	1.0	.2-*
-3	10	6	1.0	.11*
-3	10	5	1.1	1.3-*
-3	10	4	1.1	.21*
-3	10	3	4.3	3.9-
-3	10	2	5.1	4.3
-3	10	1	3.7	3.3
3	10		5.0	4.4-
3	10	1	1.1	.4-*
3	10	2	13.6	12.6-
3	10	3	10.7	9.7
3	10	4	5.2	4.5-
3	10	5	9.1	9.5
3	10	6	5.8	5.7
3	10	7	.6	3.01*
-3	11	8	2.6	2.0
-3	11	7	.7	.1-*
-3	11	6	2.5	2.7-
-3	11	5	4.2	3.2
-3	11	4	.5	.4-*
-3	11	3	5.0	5.0
-3	11	2	7.0	1.5-
-3	11	1	2.1	1.1-
3	11		1.0	.8*
3	11	1	.9	.31*
3	11	2	5.3	4.9-
3	11	3	3.4	3.5
3	11	4	.7	.5-*
3	11	5	4.3	4.4-
-3	12	6	.1	4.41*
-3	12	5	3.6	2.9-
-3	12	4	3.1	2.5
-3	12	3	.7	.41*
-3	12	2	.7	1.81*
-3	12	1	3.2	3.3
3	12		.7	.8-*
3	12	1	.6	.81*
3	12	2	.8	1.2-*
3	12	3	.4	.2
-4		14	2.2	2.7
-4		12	12.3	13.0
-4		10	1.0	1.1-*
-4		8	2.5	.91*
-4		6	9.9	8.8
-4		4	2.2	1.5-
-4		2	7.2	6.3
4			2.6	2.5
4		2	14.0	12.9-
4		4	6.2	3.8-
4		6	5.7	5.0
4		8	1.9	2.01*
4		10	1.0	3.4-
-4	1	15	.6	.31*
-4	1	14	1.2	[illegible]
-4	1	13	2.1	1.9
-4	1	12	5.0	3.9
-4	1	11	5.9	4.8
-4	1	10	9.9	9.1
-4	1	9	12.6	12.5
-4	1	8	9.2	7.5
-4	1	7	15.6	15.0-
-4	1	6	9.8	9.6
-4	1	5	22.3	22.9-
-4	1	4	3.0	3.7
-4	1	3	3.5	3.8
-4	1	2	10.6	10.6-
-4	1	1	29.1	28.9-
4	1		2.9	.7-
4	1	1	8.8	8.1-
4	1	2	6.8	6.8-
4	1	3	12.0	11.1
4	1	4	10.3	10.8
4	1	5	2.7	2.0-
4	1	6	8.8	8.3
4	1	7	1.7	.8*
4	1	8	4.7	3.7-
4	1	9	4.6	4.5-
4	1	10	2.9	3.0-
4	1	11	1.1	2.1-*
-4	2	15	1.7	1.2-
-4	2	14	4.3	2.8-
-4	2	13	1.2	.21*
-4	2	12	1.3	1.5-*
-4	2	11	2.4	1.01*
-4	2	10	7.9	7.9-
-4	2	9	2.1	1.0
-4	2	8	3.6	2.6
-4	2	7	8.6	7.5-
-4	2	6	8.2	7.6
-4	2	5	24.7	24.2-
-4	2	4	7.3	5.5
-4	2	3	19.2	18.1
-4	2	2	32.8	33.3
-4	2	1	58.2	59.2
4	2		19.3	17.9
4	2	1	19.5	19.0-
4	2	2	2.3	.4-
4	2	3	4.2	2.0
4	2	4	1.3	.2-*
4	2	5	4.2	3.6
4	2	6	2.0	1.5-
4	2	7	6.9	6.5
4	2	8	1.3	1.71*
4	2	9	5.4	5.2
4	2	10	1.0	1.31*
4	2	11	.7	2.11*
-4	3	15	.6	1.71*
-4	3	14	1.1	.7-*
-4	3	13	1.3	.41*
-4	3	12	3.7	3.1
-4	3	11	5.6	5.7-
-4	3	10	1.4	.61*
-4	3	9	4.5	3.7-
-4	3	8	9.7	8.6-
-4	3	7	2.6	2.1-
-4	3	6	4.0	4.2-
-4	3	5	5.3	4.4
-4	3	4	4.2	4.1-
-4	3	3	5.2	3.3-
-4	3	2	6.1	4.9-
-4	3	1	25.9	25.3-
4	3		1.0	.31*
4	3	1	3.8	2.3
4	3	2	1.8	.7-
4	3	3	1.2	1.21*
4	3	4	3.6	2.7
4	3	5	2.5	3.4-
4	3	6	1.4	.21*
4	3	7	10.3	9.0
4	3	8	7.4	6.7-
4	3	9	1.2	1.01*
4	3	10	2.6	2.1-
4	3	11	.6	.81*
-4	4	14	.7	.41*
-4	4	13	1.2	.5-*
-4	4	12	4.0	3.4-
-4	4	11	4.0	3.7
-4	4	10	9.0	9.4-
-4	4	9	4.9	5.1
-4	4	8	2.7	.7-
-4	4	7	2.7	2.7
-4	4	6	2.6	1.1
-4	4	5	16.2	15.1-
-4	4	4	3.0	3.8
-4	4	3	9.0	8.2-
-4	4	2	15.0	14.3
-4	4	1	1.8	1.0
4	4		2.2	1.6-
4	4	1	4.2	3.5
4	4	2	7.1	7.5
4	4	3	3.1	1.5
4	4	4	17.8	16.8
4	4	5	8.6	7.9
4	4	6	1.5	1.4-*
4	4	7	3.2	2.9
4	4	8	1.4	.11*
4	4	9	2.2	2.5-
4	4	10	3.4	4.4
-4	5	14	1.9	2.0-
-4	5	13	2.1	1.8-
-4	5	12	3.3	3.1-
-4	5	11	5.1	5.3-
-4	5	10	10.0	9.8-
-4	5	9	6.7	6.5
-4	5	8	4.7	4.6-
-4	5	7	10.4	9.5
-4	5	6	9.5	8.9
-4	5	5	5.6	5.1
-4	5	4	4.6	3.2-
-4	5	3	2.2	1.6
-4	5	2	6.0	5.2-
-4	5	1	2.7	1.2-
4	5		10.0	8.5
4	5	1	4.3	3.0
4	5	2	5.7	7.7
4	5	3	18.0	17.2-
4	5	4	11.2	10.4-
4	5	5	22.5	22.0-
4	5	6	9.1	8.7-
4	5	7	3.0	2.7-
4	5	8	1.0	.2-*
4	5	9	.9	.7-*
4	5	10	.6	.51*
-4	6	13	2.7	2.3
-4	6	12	4.3	4.4
-4	6	11	4.2	3.4
-4	6	10	2.7	3.2
-4	6	9	3.4	1.5-
-4	6	8	2.4	2.1
-4	6	7	2.5	3.0
-4	6	6	3.3	2.4
-4	6	5	7.8	6.5
-4	6	4	9.9	9.2-
-4	6	3	5.8	5.4
-4	6	2	7.5	7.0-
-4	6	1	8.0	6.7-
4	6		1.1	1.01*
4	6	1	9.4	9.0
4	6	2	5.0	4.4
4	6	3	8.8	6.0-
4	6	4	9.9	9.4
4	6	5	1.3	.51*
4	6	6	1.7	1.3-*
4	6	7	1.1	.7-*
4	6	8	3.7	3.3-
4	6	9	.7	1.9-*
-4	7	13	.6	2.01*
-4	7	12	1.7	2.0-
-4	7	11	1.0	.6-*
-4	7	10	2.3	1.0-
-4	7	9	3.7	2.8
-4	7	8	3.0	2.3
-4	7	7	8.0	7.6-
-4	7	6	13.1	11.5
-4	7	5	9.5	7.5-
-4	7	4	7.4	6.6
-4	7	3	1.3	.8-*
-4	7	2	3.6	3.2
-4	7	1	7.9	7.0-
4	7		2.9	1.0
4	7	1	5.6	4.5-
4	7	2	4.6	4.3
4	7	3	1.2	.71*
4	7	4	4.3	3.9-
4	7	5	1.3	1.0-*
4	7	6	1.5	1.9-
4	7	7	1.0	1.51*
4	7	8	2.3	1.8
4	7	9	.6	2.21*
-4	8	12	.6	.8-*
-4	8	11	.7	.61*
-4	8	10	2.2	2.6
-4	8	9	1.0	.2-*
-4	8	8	4.3	3.8
-4	8	7	12.5	12.0
-4	8	6	7.6	5.8
-4	8	5	5.5	6.0
-4	8	4	1.7	1.7-*
-4	8	3	2.6	2.1-
-4	8	2	6.9	6.0
-4	8	1	1.2	2.5-*
4	8		11.5	11.5
4	8	1	4.0	4.2
4	8	2	2.8	1.8
4	8	3	4.4	3.6-
4	8	4	3.8	2.7
4	8	5	2.5	1.7
4	8	6	.9	.21*
4	8	7	5.1	4.0
4	8	8	.6	2.9-*
-4	9	11	.6	2.31*
-4	9	10	.7	.4-*
-4	9	9	2.0	2.3-
-4	9	8	9.3	9.3-
-4	9	7	11.8	11.6-
-4	9	6	10.6	9.6-
-4	9	5	5.0	3.9-
-4	9	4	3.6	2.4-
-4	9	3	1.7	1.1
-4	9	2	3.5	2.3
-4	9	1	1.2	1.0-*
4	9		6.9	5.8-
4	9	1	1.2	.11*
4	9	2	3.3	3.0-
4	9	3	2.3	1.2
4	9	4	1.0	.5-*
4	9	5	4.4	3.6
4	9	6	.7	.21*
4	9	7	.6	4.71*
-4	10	9	.6	.6-*
-4	10	8	2.1	1.3
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-4	10	3	1.1	.11*
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-4	10	1	3.4	2.9
4	10		3.6	2.8-
4	10	1	3.2	2.9
4	10	2	3.7	3.4-
4	10	3	2.0	1.7
4	10	4	9.3	5.4
4	10	5	3.1	3.6
-4	11	7	7.3	7.1-
-4	11	6	3.7	3.9-
-4	11	5	7.4	6.1
-4	11	4	11.0	9.0-
-4	11	3	2.7	2.6
-4	11	2	5.5	5.7-
-4	11	1	2.0	1.9-
4	11		4.1	3.7-
4	11	1	2.6	2.8-
4	11	2	.7	.7-*
4	11	3	6.2	5.7-
-5		14	.8	.41*
-5		12	2.7	1.8-
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-5		8	2.1	2.5-
-5		6	2.8	1.8-
-5		4	15.6	14.8-
-5		2	6.1	4.9-
5			6.5	5.9-
5		2	4.1	1.7
5		4	14.2	13.0
5		6	1.1	3.11*
5		8	1.6	.7-*
-5	1	15	.5	.91*
-5	1	14	.5	[illegible]
-5	1	13	2.0	1.6
-5	1	12	9.6	10.4
-5	1	11	15.8	16.4
-5	1	10	12.6	13.3
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-5	1	7	5.8	4.3-
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5	1	4	9.5	8.2
5	1	5	1.6	.51*
5	1	6	1.4	.91*
5	1	7	3.0	2.6-
5	1	8	1.6	[illegible]
5	1	9	1.1	1.5-*
5	1	10	.9	.71*
-5	2	15	.6	3.61*
-5	2	14	1.9	1.8-
-5	2	13	1.1	[illegible]
-5	2	12	3.3	3.7-
-5	2	11	3.6	3.1-
-5	2	10	6.1	6.0-
-5	2	9	3.3	2.7
-5	2	8	1.8	1.0-
-5	2	7	7.6	6.4-
-5	2	6	5.6	3.9
-5	2	5	10.0	9.5-
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-5	2	3	12.6	12.6
-5	2	2	5.3	4.5
-5	2	1	22.1	22.4
5	2		12.6	12.3-
5	2	1	9.3	9.9-
5	2	2	1.2	.61*
5	2	3	1.3	.3-*
5	2	4	7.6	7.1
5	2	5	2.7	2.8
5	2	6	1.3	.71
5	2	7	3.5	3.2
5	2	8	4.5	4.2
5	2	9	.9	.61*
5	2	10	.6	.91*
-5	3	14	4.2	3.5-
-5	3	13	1.1	.9-*
-5	3	12	3.0	3.0
-5	3	11	1.4	1.3-*
-5	3	10	7.1	7.3
-5	3	9	5.4	4.4-
-5	3	8	2.0	1.4-
-5	3	7	3.6	4.8
-5	3	6	1.9	2.2-
-5	3	5	6.6	5.7
-5	3	4	2.9	2.1-
-5	3	3	4.4	4.0-
-5	3	2	4.3	3.3-
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5	3		3.4	2.9-
5	3	1	13.7	12.6
5	3	2	1.2	.5-*
5	3	3	3.3	2.5-
5	3	4	4.0	1.5
5	3	5	3.0	3.0
5	3	6	3.7	3.2
5	3	7	3.8	4.1-
5	3	8	4.5	4.3
5	3	9	3.1	2.8-
-5	4	14	.6	.6-*
-5	4	13	1.1	.71*
-5	4	12	3.5	4.3-
-5	4	11	1.4	.5-*
-5	4	10	1.5	1.0-*
-5	4	9	2.5	4.0-
-5	4	8	1.0	1.2-
-5	4	7	10.0	10.6-
-5	4	6	10.2	9.1-
-5	4	5	4.7	3.0-
-5	4	4	4.7	3.3-
-5	4	3	4.5	3.4-
-5	4	2	1.3	.61*
-5	4	1	1.3	1.11*
5	4		3.9	2.2-
5	4	1	2.7	1.4-
5	4	2	6.7	6.4
5	4	3	8.0	7.7
5	4	4	1.5	1.11*
5	4	5	4.3	4.2-
5	4	6	2.2	2.2-
5	4	7	8.9	9.4-
5	4	8	6.2	5.7
5	4	9	4.0	3.8-
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-5	5	11	1.0	1.81*
-5	5	10	1.1	.6-*
-5	5	9	2.3	1.9-
-5	5	8	1.1	.11*
-5	5	7	11.2	11.6
-5	5	6	3.7	4.2-
-5	5	5	15.6	15.0
-5	5	4	4.3	4.3-
-5	5	3	2.0	1.7-
-5	5	2	4.7	3.8-
-5	5	1	2.0	.8
5	5		6.6	6.1
5	5	1	4.6	3.1-
5	5	2	1.1	.91*
5	5	3	11.8	11.7-
5	5	4	9.4	8.8-
5	5	5	5.5	5.7-
5	5	6	1.0	.8-*
5	5	7	5.6	6.7-
5	5	8	.7	2.31*
5	5	9	.2	2.7-*
-5	6	13	1.5	1.7-
-5	6	12	.8	.3-*
-5	6	11	2.2	2.4-
-5	6	10	1.0	.9-*
-5	6	9	2.0	3.2-
-5	6	8	1.1	.91*
-5	6	7	6.5	6.6
-5	6	6	15.0	15.6-
-5	6	5	22.6	25.2
-5	6	4	15.6	14.7-
-5	6	3	6.3	6.1
-5	6	2	2.7	1.8
-5	6	1	7.0	6.7-
5	6		3.8	2.5
5	6	1	1.1	.9-*
5	6	2	1.1	[illegible]
5	6	3	4.4	3.9
5	6	4	1.1	.91*
5	6	5	1.0	.11*

Table 5 (*cont.*)

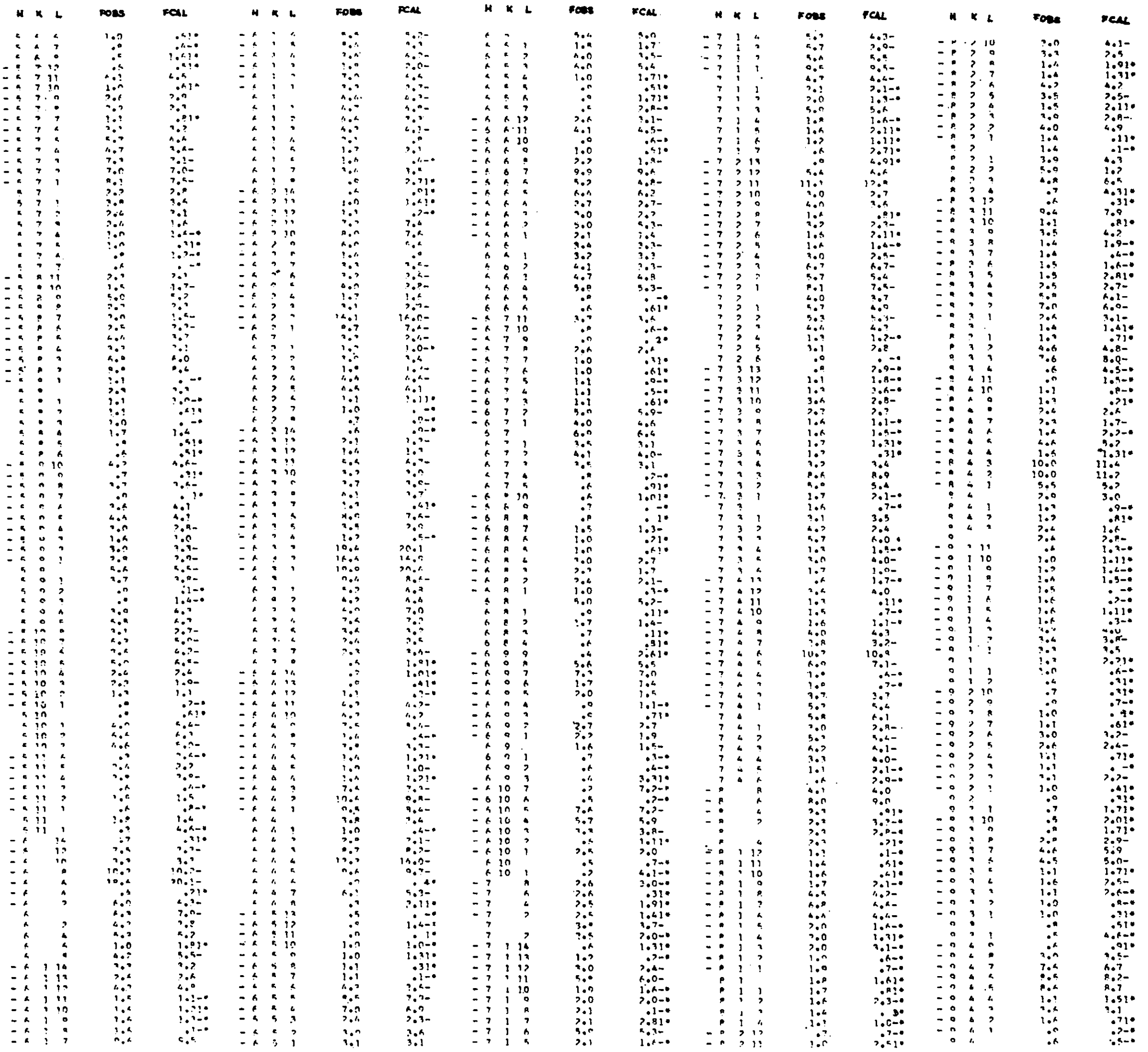

Table 6. *Hydrogen atom parameters*

	x/a	*y/b*	*z/c*	$\hat{B}$
H[O(1)]	−0·234 (7)	0·051 (5)	−0·084 (5)	4·57
H[C(2)]	0·135 (7)	0·347 (5)	−0·119 (5)	3·12
H[C(6)]	0·234 (7)	0·305 (5)	0·235 (5)	3·06
H[C(7)]	0·375 (7)	0·632 (5)	−0·130 (5)	4·36
H[C(7)]	0·225 (7)	0·531 (5)	−0·194 (5)	4·36
H[C(7)]	0·163 (7)	0·663 (5)	−0·149 (5)	4·36
H[C(8)]	0·259 (7)	0·768 (5)	0·062 (5)	4·98
H[C(8)]	0·382 (7)	0·748 (5)	0·178 (5)	4·98
H[C(8)]	0·442 (7)	0·724 (6)	0·068 (4)	4·98
H[C(9)]	0·475 (7)	0·588 (6)	0·322 (4)	5·27
H[C(9)]	0·342 (7)	0·469 (5)	0·362 (5)	5·27
H[C(9)]	0·260 (7)	0·614 (5)	0·305 (5)	5·27

acids (von Krausse & Dunken, 1966; Ferguson & Islam, 1966) are respectively 53°31′, 48°31′, 18°3′, 13°7, and 6°7′ which illustrates the influence of methyl groups in the *ortho* positions. There is no evidence of any such bond interactions in the present structure.

A feature which is common in most carboxyl derivatives, *i.e.* dimerization by double hydrogen bonds between two carboxyl groups around the symmetry centres, is observable in the present structure. The value found for the H-bond distance of $2{\cdot}62_8$ Å is normal.

Intermolecular distances of less than 4 Å have been calculated and are shown in Table 3 (Fig. 2). They are normal.

Fig. 1 illustrates the packing of the molecules; they form chains oriented along lines defined by C(10)–C(10)(XI) and C(10)(VI)–C(10)(X), with van der Waals forces providing cohesion between dimers.

All calculations were made on the IBM 7070 and 7090 computers of the Centro de Cálculo Electronico of the C.S.I.C. (Madrid, Spain). The present work is part of a Doctoral Thesis by one of us (F.H.C.).

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The Crystal Structure of a 1:1 Cupric Nitrate–Pyrazine Complex $Cu(NO_3)_2.(C_4N_2H_4)$

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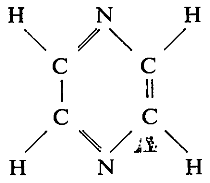
The crystal structure of a 1:1 cupric nitrate–pyrazine complex, $Cu(NO_3)_2.(C_4N_2H_4)$, was determined by single-crystal X-ray diffraction techniques. This compound crystallizes in the orthorhombic system with $a=6{\cdot}712$, $b=5{\cdot}142$, and $c=11{\cdot}732$ Å, space group *Pmna*, $\varrho=2{\cdot}19$ g.cm^{-3} and $Z=2$. The intensities of 642 unique reflections were recorded by the 2θ-scan method and the structure was solved by an analysis of the three-dimensional Patterson map. The structure is a coordination polymer and consists of linear –Cu–pyrazine–Cu–pyrazine– chains. The nitrate groups lie in mirror planes normal to the chain axes and they are coordinated to the Cu^{II} ion unsymmetrically through two oxygen atoms. Refinement by anisotropic least-squares analysis gave an R value of 0·04.

Introduction

Aromatic rings which contain pyridine type nitrogen atoms ($\gtrdot$N) coordinate to transition metal ions. If the coordinating molecule contains more than one pyridine type nitrogen atom, bonding may occur to more than one metal ion to form a polynuclear species. Pyrazine (1,4-diazine)



and $Cu(NO_3)_2$ form an anhydrous crystalline complex with a 1:1 pyrazine to $Cu(NO_3)_2$ ratio. In pyrazine, equivalent nitrogen atoms occupy opposite vertices in the ring and a 1:1 composition suggests chains of the type –pyrazine–Cu–pyrazine–Cu–. As Cu^{II} is generally fourfold or sixfold coordinated, the nitrate groups must be involved in the coordination to the metal ion. The structure analysis of the complex was undertaken to elucidate the features of the copper–ring linkage and to determine the role of the nitrate groups in the coordination about the copper ion.

Experimental

Crystals of $Cu(NO_3)_2.(C_4N_2H_4)$ were grown by evaporation of an aqueous solution of cupric nitrate and pyrazine. Crystal symmetry and approximate cell parameters were determined from zero and upper level precession photographs. Systematic extinctions ($h0l$: $h+l=2n+1$; $hk0$: $h=2n+1$) indicate that the space group is either *Pmna* (No. 53) or *P2na* (No. 30). The centric space group was assigned on the basis of the complete structure determination.

To determine precise unit-cell parameters, the 2θ angles of a set of eighteen reflections were measured on a single-crystal diffractometer using molybdenum radiation ($\lambda=0{\cdot}71068$ Å). The cell parameters were then refined by least-squares analysis to obtain the best agreement between the calculated and observed 2θ