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The Crystal Structure of 4,4-*trans*-Azopyridine-N-Oxide*

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Investigation of this azo-derivative was undertaken as a sequel to that of the 4-nitro-compound (Eichhorn, 1956*a*). Whereas marked quinoidal character was found in the nitro-derivative, resonance of aromatic ring character appears to be restored to the pyridine ring by diazotization. A three-dimensional refinement of the crystal structure was carried to a percentage discrepancy of $R_{21\Omega} =$ 15·2%, with e.s.d. values for the atomic positions ranging between 0·0044 and 0·0096 Å. The molecule is flat, with the azo bond across a center of symmetry, which was chosen as origin. The space group is $P2_1/n$; there are two molecules per unit cell.

Introduction

A general survey of pyridine-N-oxide derivatives was started some time ago in an effort to provide theoretical chemists with accurate experimental data of these intermediates which are important in synthetic chemistry (Eichhorn & Hoogsteen, 1957). Very little moreover is known of the stereochemistry of azopyridines and almost nothing of azopyridines in which the azo bond occurs at the para position (LeFevre & Worth, 1951; Friedl, 1913). In the course of a preliminary study of the compound, now to be described in detail, it became certain that features observed in the bond lengths of the 4-nitropyridine-N-oxide (Eichhorn, 1956*a*, *b*) must be absent in the azo derivative; a precise analysis was therefore undertaken.

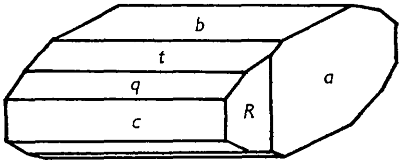

Fig. 1. Morphology of investigated crystal of *trans* 4,4′-azo-pyridine-N-oxide.

4,4′-trans-azopyridine-N-oxide is obtained through reduction and diazotization from 4-nitropyridine-N-oxide, and it is then purified by repeated recrystallization from a mixture of ethanol and acetone. Beautiful strongly dichroic, blood red needles, elongated parallel to the monoclinic *a*-axis are thus obtained. Their decomposition point is 243 °C. (Ochiai, 1953). A morphological examination showed the forms {100}, {010}, {001}, {011}, {021} and {$\bar{1}$01} to be well developed; the crystals are monoclinic prismatic, with Laue symmetry C_{2h} (Fig. 1). The beta angle was determined crystallometrically and then confirmed from X-ray photographs. The cell data were deduced from oscillation and Weissenberg photographs, taken about the three principal axes; the density of the substance was measured by flotation.

Cell data:

Systematic absences follow from:

$$(0k0) \text{ for } k = 2n$$
$$(00l) \text{ for } l = 2n$$
$$(h0l) \text{ for } h+l = 2n.$$

This establishes the space group unequivocally as $P2_1/n\text{–}C^5_{2h}$.

$$\left.\begin{array}{l} a = 4{\cdot}56 \\ b = 11{\cdot}75 \\ c = 9{\cdot}75 \end{array}\right\} \pm 0{\cdot}02\ \text{Å}$$

(Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å)

beta = 114° 7′ ± 3′

$V = 477 \pm 2$ Å^3

$d_f = 1{\cdot}497$ g.cm.$^{-3}$; $d_x = 1{\cdot}504$ g.cm.$^{-3}$.

There are two molecules per unit cell, with equivalent positions:

$$(x, y, z) \text{ and } (\bar{x}, \bar{y}, \bar{z});$$
$$(\tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{1}{2}+z) \text{ and } (\tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{1}{2}-z).$$

Diffraction data

To stabilize the compound, all investigations were carried out in a refrigerated room kept at −10 °C. The target used was copper, and the Weissenberg instrument a Von der Heide equi-inclination camera adapted for operation in the medium low temperature range. Cooling of the anode is achieved by a closed circuit pumping unit utilizing a silicone oil. The

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maximum skew of the camera is about 35 degrees under normal operating conditions, permitting us to record the four lowest levels about the short *a*-axis of the compound. However the (4*kl*) layer was also obtained as a general inclination photograph and indexed with the help of an equi-inclination picture taken with a Supper instrument at room temperature. The highest layer, (5*kl*) could not be photographed in this way, nor were any reflexions with $h=5$ found on recordings about the two other principal axes, as their intensity had died down owing to heat movement.

To adjust all layers to the same scale, cross layers about another axis were used. The multiple-film-visual-estimation technique was employed. Processing of the crude intensity data to yield *F*-values was carried out with the aid of punched card equipment. 600 out of the possible 995 reflexion spots within the recorded layers were observed with a crystal of about 0·2 mm. diameter, and with exposure times of the order of 30 hrs.

The trial structure

When we received the sample of 4,4′-azopyridine-N-oxide, no information regarding its stereochemistry accompanied it. However it follows from the X-ray data that the molecule must possess a center of symmetry, which excludes the *cis* isomer. An effort was made to obtain this *cis* isomer by long ultraviolet irradiations from a high pressure mercury arc. Fairly concentrated acetone solutions of the *trans* isomer were used as the starting substance. Fractional crystallization of the irradiated liquid at low temperatures and in the dark yielded a deep-orange substance, crystallizing in very fine needles, elongated in its monoclinic *b*-axial direction. Cell data at hand suggest that this is the *cis* isomer. It can readily be converted into the *trans* isomer by redissolution (Eichhorn & Hoogsteen, 1957).

In the geometrical *trans* isomer the azo bridge is positioned across a center of symmetry which is chosen as origin of the grid. In the set of zero layer data, the (202) plane is by far the most outstanding in intensity; its first order plane is extinguished through space-group symmetry, but it would have a separation of $d_{101}=3·27$ Å. This value is of the order of thickness that one would expect for a flat resonance structure. In the three-dimensional data set the (111) plane is by far the most notable, but its second order plane (222) has a lesser intensity than (202); $d_{111}=3·15$ Å. It was expected that the plane containing the molecules would indexwise occupy a position between (101) and (111). For a start the (101) plane was assumed to be this molecular plane and a model of the molecule was revolved within this plane to give satisfactory packing and be consistent with respect to other fairly strong reflexions. The model thus obtained proved to be correct in essence and refined smoothly.

The projection || *a*

The (0*kl*) projection, because of the short *a*-axis, gave full resolution. It was first refined as a preliminary to three-dimensional operations. Differential syntheses with compensation for termination-of-series errors (backshift) were utilized. Heat movement was assumed to be of the ideal isotropic type (Eichhorn, 1956*b*). Four successive refinement cycles reduced the percentage discrepancy of the projectional structure amplitudes to about 15% for the complete set. In the fifth cycle hydrogen atoms were included at 0·95 Å radial distance from their carbon atoms. This diminished R_{21}* to about 14%. A final refinement cycle for the projection resulted in $R_{21\Omega}=11·9\%$. Fig. 2 shows the projection at this stage. The heterocyclic ring is seen to be somewhat distorted from an axially symmetric model, undoubtedly owing to the presence of the azo bridge. In the 4-nitro-pyridine-N-oxide the ring is axially symmetric.

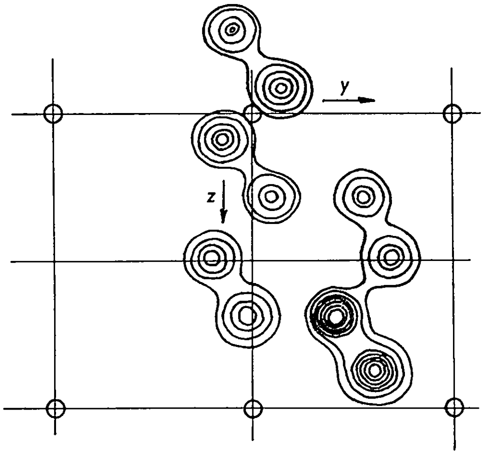

Fig. 2. The (0*kl*) electron-density projection at $R_{21\Omega}=11·9\%$. Contours are drawn at equally spaced but arbitrary intervals.

Three-dimensional refinement

On the basis of likely bond lengths, and the *y* and *z* parameters derived from the || *a* projection, a three-dimensional model was constructed and further refined using all available reciprocal lattice data. The same refinement technique as for the projection was employed. Four cycles were necessary to attain an $R_{21\Omega}=15·2\%$ for the three-dimensional set of structure factors. Refinement was discontinued when compensated shifts dropped below 0·003 Å and the curvatures remained constant. After each refinement cycle all bond lengths were calculated (with punched card equipment) to aid in a diligent evaluation of the new atomic positions. Since the positional shifts are some-

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* For an explanation of the R_{21} and $R_{21\Omega}$ nomenclature, see Eichhorn (1956*a*).

times, in early stages, arithmetically exaggerated (because of the low curvature values in the denominator of the formulae) it was found necessary to reduce the calculated shifts to sensible values. Empirically a scheme was worked out whereby a certain percentual reduction of a computed parameter shift was introduced, based upon the computed curvature of the atom at this stage and the magnitude of the calculated shifts (Eichhorn, 1956*b*). We were greatly aided by numerical data at hand, collected in refinement of the nitro-derivative. Optimization procedures were used throughout refinement (Eichhorn, 1956*a*).

An adaptation of the Cruickshank formula (Cruickshank, 1949) was employed for derivation of e.s.d. values; the formula for this space group becomes:

$$\sigma_x = (a/2_\pi)\cdot\frac{(\Sigma_H h^2 . \Delta F^2)^{\frac{1}{2}}}{\Sigma_H h^2 F\cdot\cos\left(hx+lz+\dfrac{k+l}{4}\right)\cdot\cos\left(ky-\dfrac{k+l}{4}\right)}$$

and its cyclic equivalents for the other coordinates. The values found are listed below:

	σ_x (Å)	σ_y (Å)	σ_z (Å)
Oxygen	0·0044	0·0084	0·0073
Nitrogens	0·0051	0·0087	0·0079
Carbons	0·0057	0·0096	0·0082

The standard deviation of the electron density was calculated to be $\sigma_L = 0{\cdot}089$ e.Å^{-3}.

Heat movement

Since we would then have about twenty observational data per parametric constant introduced, we would have been justified to assign individual Debye–Waller constants to each atom, thus creating the non-ideal isotropic case (Eichhorn, 1956*b*). No need presented itself for such a procedure however, with the possible exception of the oxygen atom. The optimal Debye–Waller constant was calculated to be $B_\Omega =$ 2·90 Å^2. In order to assess the situation properly the peak-heights and peak-height residuals at the atomic centers were computed:

Atom no.	Type	$(\varrho_i)_{F_o}$	$(\varrho_i)_{F_o}-(\varrho_i)_{F_c}$
1	oxygen	13·84 e.Å^{-3}	$-$1·27 e.Å^{-3}
2	nitrogen	13·37	zero
3	carbon	11·67	+0·29
4	carbon	11·73	+0·23
5	carbon	11·99	+0·64
6	carbon	11·69	$-$0·06
7	carbon	11·65	$-$0·23
8	nitrogen	13·38	+0·44

It is difficult to judge to what extent the residuals are caused by individual elastic constants of the atoms, individual charge distributions or uncertainty (inaccuracy) in the observational intensity set. To introduce anisotropy of heat movement would no doubt improve the agreement of the structure factors, but would have only slight theoretical justification. One has to bear in mind, however, that a better agreement of structure factors will lower the e.s.d. values of the atomic positions. A probing procedure (rather than calculating a set of density sections) was adopted to find out whether the density peaks had elliptical shape. Densities were calculated around a spherical shell of all atoms under investigation, at 0·7 Å distance from the core. The six values computed per atom did in no case differ sufficiently from each other to be in any way significant. We found very good agreement between the densities so obtained and those computed with the aid of the Booth–Costain formula.

Non-observed planes in the three-dimensional set were accounted for computationally in the following way: half the minimum observable intensity was assigned to all these absent planes, and their artificial amplitude deduced therefrom. Whenever F_c was lower than this value, F_o was set equal to F_c in all subsequent operations of the cycle. If F_c was larger than the artificial threshold value, F_o was set equal to this F_t, and the difference ΔF accounted for in calculation.

Table 1 records the observed data and the corresponding values calculated from the final structure and the Debye–Waller constant. The scattering factors used were those of Berghuis *et al.* (1955).

Discussion of the structure

The atomic positions, as they emerged from the final three-dimensional refinement cycle are listed hereunder:

Atom No.	Type	x	y	z
1	oxygen	0·5358	0·1503	0·4373
2	nitrogen	0·6388	0·1074	0·3440
3	carbon	0·6903	$-$0·0058	0·3414
4	carbon	0·8061	$-$0·0494	0·2433
5	carbon	0·8622	0·0195	0·1417
6	carbon	0·7968	0·1344	0·1428
7	carbon	0·6915	0·1763	0·2437
8	nitrogen	0·9828	$-$0·0327	0·0454

The bond data computed from the unit cell and these positions can be found in Fig. 3. The molecule, as one might have expected, is flat and contained within a general plane of best fit, expressed by the relationship:

$$1{\cdot}009x+0{\cdot}506y+0{\cdot}877z=1{\cdot}000 .$$

Upon introducing the fractional indices of this plane in the formula for $\sin^2\theta$, one arrives at a value $d_M =$ 3·31 Å for the separation of the plane, which is entirely consistent with the structure. The elevation of atoms above this plane can now be found from the expression:

$$T_i = d_M . (1{\cdot}009x_i+0{\cdot}506y_i+0{\cdot}877z_i-1{\cdot}000) \text{ in Å} .$$

Only the elevation of atom 8, the nitrogen of the azo bond, is possibly significant, it being $T_8 = +0{\cdot}033$ Å.

The e.s.d. values of intramolecular bonds and angles are given below. If we accept the theory of significance evaluation, propounded by various authors (e.g.

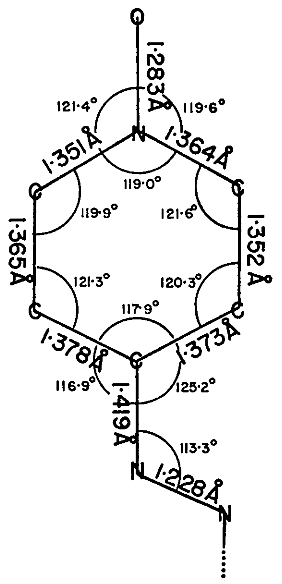

Fig. 3. Bond lengths and angles as found from the final set of 3-dimensionally refined atomic positions.

Jeffrey & Cruickshank, 1953), this implies that differences of comparable bonds may be taken as realistic only if they exceed the e.s.d. value of the bonds, σ_L, by a factor t. The value t is generally taken to be between 2·5 and 3·2; we have adopted the lower bound $t=2{\cdot}5$, since we did not want to compensate for peak-height residuals (this would after all not have affected the atomic positions, only the goodness-of-fit of the structure factor set).

When the atoms that form the bond, the σ-value of which one wishes to determine, lie in general positions and $\sigma_x \neq \sigma_y \neq \sigma_z$ for these atoms, the evaluation of σ_L involves an adaptation of the 'bond-length formula' in the following approximation for the monoclinic case:

$$\sigma^2 = (\Delta x\,.\,\sigma_x)^2 + (\Delta y\,.\,\sigma_y)^2 + (\Delta z\,.\,\sigma_z)^2 - 2\,.\,(\Delta x\,.\,\Delta z\,.\,\sigma_x\,.\,\sigma_z\,.\cos\beta)/L^2,$$

where $\Delta x = x_i - x_j$, $\sigma_x = (\sigma_x)_i$ and σ_i = e.s.d. of atom i in the bond direction. L = bond length.

Then $\sigma_L^2 = \sigma_i^2 + \sigma_j^2$ for all bonds except the azo bridge where both nitrogens are related by a center of symmetry; there $\sigma_L = 2\,.\,\sigma_N$. The computation of e.s.d. values for the bond angles can be developed along these same lines. These values, however, differed so slightly in our case, that we averaged them to read: $\sigma_{\measuredangle} = 0{\cdot}55°$ for all bonds.

Bond	Type	L (Å)	σ_L (Å)
1–2	N–O	1·283	0·011
2–3	C–N	1·351	0·016
2–7	C–N	1·364	0·012
3–4	C–C	1·365	0·012
6–7	C–C	1·352	0·013
4–5	C–C	1·378	0·012
5–6	C–C	1·373	0·011
5–8	C–N	1·419	0·012
8–8′	N–N	1·228	0·015

We see that comparable bonds within the molecule do not differ significantly, i.e. the pairs 2–3 & 2–7, 3–4 & 6–7, 4–5 & 5–6. However, the C–N bond 5–8 is significantly longer than the ring C–N bond. The e.s.d. value for the bonds is small and on the basis of the assumed significance levels permits us to draw the conclusion that the hexagon is not mirror-symmetric along the 1–2–5–8 axis.

The N–O bond in the 4-nitropyridine-N-oxide structure is shorter than in the azo derivative, the difference being possibly significant (1·260 and 1·283 Å). The C–N bond 5–8 is significantly longer in the nitro-compound (1·472 and 1·419 Å). The C–C bonds 3–4 and 6–7 are significantly longer in the azo structure and the C–N bonds 2–3 and 2–7 significantly shorter than in 4-nitropyridine-N-oxide. The C–C bonds 4–5 and 5–6 are also significantly shorter in 4,4′-*trans*-azopyridine-N-oxide. The N–N bond of the azo bridge is probably almost a pure double bond and is of the same length as found e.g. in *trans* and *cis* azo benzene (Robertson, 1939) and (De Lange *et al.*, 1939).

We note that the structural evidence appears to point to the conclusion that despite oxidation of the pyridinic nitrogen, quinoidal character of the ring of the parent substance (4-nitropyridine-N-oxide) has been removed by diazotization, and that the azo derivative shows more aromatic behaviour.

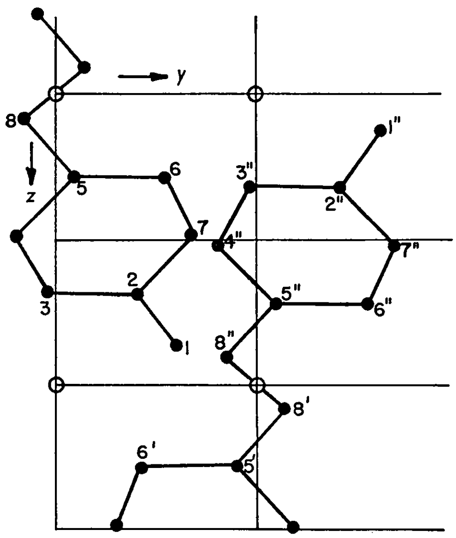

Fig. 4. Grouping of molecules in the unit cell, as seen along the a-axis; numbering of atoms is for the table of intermolecular distances.

The nearest intermolecular approach distances were calculated to find possible unusual interactions. Those, however, were absent, as may be seen from the list given (p. 754):

Table 1. F_o *and* F_c *values*

kk	*ll*	F_o	F_c
h=0			
00	02	29·2	−27·3
	04	10·6	−9·1
	06	1·2	−1·8
	08	4·0	3·7
	10	18·7	−19·7
01	01	8·4	7·4
	02	13·5	17·0
	03	11·5	12·1
	04	16·5	18·0
	05*	0·6	0·6
	06	9·7	9·4
	07*	0·2	0·2
	08*	1·2	1·2
	09	3·8	5·2
	10	2·8	−4·0
	11	4·6	−5·8
02	00	59·0	60·3
	01	50·8	−53·8
	02	1·2	−2·0
	03	20·8	−19·0
	04	14·5	−11·5
	05	10·6	8·8
	06	12·4	10·9
	07	3·6	−1·8
	08	2·3	1·4
	09	3·6	−4·3
	10	8·0	−6·8
	11	3·4	5·6
03	01	32·4	33·3
	02	12·1	13·6
	03	22·0	20·4
	04	6·6	6·9
	05	5·5	−4·5
	06	12·8	9·1
	07	8·0	−8·3
	08	3·4	1·5
	09	3·8	−4·7
	10*	1·1	−1·1
	11	1·9	−2·8
04	00	8·0	−8·3
	01	34·1	28·3
	02	2·1	−1·2
	03	3·0	−7·8
	04	4·4	5·5
	05	24·3	28·9
	06	2·1	2·9
	07	4·4	−3·6
	08	2·3	1·7
	09	3·0	4·7
	10*	0·3	0·3
05	01	13·6	13·6
	02	6·3	−5·2
	03	1·7	−1·9
	04	5·3	−5·3
	05	2·6	0·3
	06	3·0	1·3
	07*	0·3	0·3
	08	2·1	0·0
	09*	0·7	−0·7
	10	3·2	4·7
06	00	35·5	36·0
	01	24·5	24·5
	02	2·3	4·3
	03	11·9	11·5
06	04	4·6	−2·0
	05	7·5	6·4
	06	2·8	−2·9
	07	6·3	5·3
	08*	0·5	−0·5
	09	3·8	4·4
	10	4·0	−5·8
07	01	5·5	−6·6
	02	8·7	−4·2
	03	6·4	−5·6
	04	17·7	16·5
	05	2·1	−0·6
	06	8·2	9·3
	07	7·2	7·1
	08	3·0	−2·4
	09	1·7	3·3
08	00	11·7	12·5
	01*	0·5	−0·5
	02	3·8	4·0
	03	3·4	−5·3
	04	21·7	−19·0
	05	2·3	0·2
	06	16·5	13·7
	07	4·4	3·7
	08	2·8	−2·5
	09	1·0	1·1
09	01	3·0	−1·2
	02	4·4	−3·8
	03	8·2	8·3
	04	15·1	13·4
	05	6·3	−5·1
	06	14·7	11·9
	07	2·6	−2·8
	08	3·0	−3·4
	09	1·0	1·1
10	00	5·7	−5·4
	01	2·8	−1·4
	02	4·0	−5·4
	03	4·4	4·0
	04	10·1	−8·2
	05	14·0	12·3
	06	11·5	10·1
	07*	0·0	0·0
	08	1·0	0·8
11	01	4·4	−4·2
	02	2·8	−2·8
	03	6·6	6·5
	04*	0·8	−0·8
	05	1·2	−1·8
	06	3·6	1·9
	07	4·6	−4·8
12	00	3·2	−2·1
	01	4·6	−4·1
	02	2·8	−1·3
	03	7·7	7·4
	04	2·1	−0·7
	05	3·8	3·9
	06*	0·4	0·4
13	01	5·1	−5·7
	02*	0·2	0·2
	03	2·6	−2·3
	04*	0·5	0·5
	05*	0·1	0·1
14	00	3·2	−2·6
	01	3·0	−2·6
	02	1·2	2·2
	03	1·7	1·3
h=1			
00	00	8·0	−8·0
	01*	0·0	0·0
	02	5·1	2·0
	03*	0·0	0·0
	04	6·6	5·3
	05*	0·0	0·0
	06*	0·1	−0·1
	07*	0·0	0·0
	08*	0·6	0·6
	09*	0·0	0·0
	10	2·4	4·9
01	00	40·8	41·5
	01	111·9	115·0
	02	27·1	−28·5
	03	7·3	−7·2
01	04	9·5	−9·5
	05	10·3	−9·7
	06	2·6	0·6
	07	2·0	0·8
	08*	0·6	0·6
	09	2·7	2·5
	10	1·8	−1·9
02	00	37·0	35·1
	01	24·1	21·4
	02	3·5	8·6
	03	6·7	11·0
	04	11·2	13·1
	05	7·9	9·6
	06	4·1	−4·5
	07	4·6	5·6
	08	1·9	−2·5
	09	2·1	2·1
	10*	1·1	−1·6
03	00	4·9	5·7
	01	2·6	−2·3
	02	2·9	−5·4
	03*	1·2	−1·2
	04	10·6	−10·5
	05	2·5	−0·7
	06	14·8	13·8
	07	4·2	6·1
	08	3·0	−2·6
	09*	0·7	0·7
	10*	0·2	0·2
04	00	34·9	35·7
	01	2·6	−1·5
	02	11·3	13·7
	03	2·6	1·5
	04	2·9	3·1
	05	1·8	−2·9
	06*	0·8	−0·8
	07	3·7	3·2
	08	2·9	−3·9
	09*	0·2	0·2
	10*	1·1	−3·6
05	00	31·8	−29·1
	01	14·2	14·6
	02	27·2	24·9
	03*	1·1	−1·3
	04	8·0	8·7
05	05*	1·1	2·2
	06	11·1	12·1
	07*	1·1	−2·2
	08*	1·2	−1·2
	09*	1·0	1·0
06	00	2·8	−4·0
	01	2·1	2·5
	02	3·8	4·0
	03	7·2	−6·8
	04	6·3	−6·8
	05	8·7	7·0
	06	3·3	3·1
	07*	0·5	0·5
	08	1·5	2·3
	09*	0·2	−0·2
07	00	7·6	−5·9
	01	24·5	23·4
	02	7·5	6·3
	03	5·0	7·0
	04	3·7	3·3
	05	10·4	−11·6
	06*	0·3	−0·3
	07	3·7	2·9
	08	3·0	3·3
	09*	0·8	0·8
08	00	4·7	4·4
	01	7·7	5·3
	02	3·6	−2·8
	03	5·7	−3·1
	04	2·0	2·8
	05	13·6	13·6
	06	4·0	−3·3
	07	6·6	7·1
	08*	1·1	1·9
09	00	1·9	1·7
	01*	0·5	−0·5
	02*	0·5	−0·5
	03*	0·7	0·7
	04	4·6	−6·6
	05	11·9	−11·2
	06	7·0	5·8
	07	8·7	10·1
	08*	1·2	1·2
10	00	2·7	−1·7
	01*	0·6	0·6
	02	2·7	−1·7
	03	2·7	−1·8
	04	5·5	5·1
	05	2·4	1·9
	06*	1·1	−1·5
	07	6·1	6·2
11	00	3·3	3·0
	01	3·3	−2·9
	02*	1·2	−1·2
	03	4·3	−4·2
	04	2·9	3·1
	05	2·6	−1·1
	06	5·6	6·9
12	00	6·7	−6·5
	01*	0·1	−0·1
	02	4·1	−4·6
	03*	1·0	−1·0
	04*	0·2	−0·2
	05*	0·7	−0·7

Table 1 (*cont.*)

kk	*ll*	F_o	F_c
13	00	3·8	3·7
	01	3·0	−1·6
	02	4·6	−4·2
	03*	1·1	2·2
	04	4·6	5·5
14	00	2·2	−2·7
	01	1·7	−0·4
	02	2·6	−3·2
	03	3·5	3·0
$h=-1$			
00	01*	0·0	0·0
	02	5·3	6·1
	03*	0·0	0·0
	04	4·5	5·1
	05*	0·0	0·0
	06	6·1	5·3
	07*	0·0	0·0
	08	8·7	10·6
	09*	0·0	0·0
	10	7·5	−7·8
	11*	0·0	0·0
	12*	1·1	−1·6
01	01	18·1	−18·5
	02	13·9	11·8
	03	10·6	−9·3
	04	0·9	0·9
	05	12·8	10·1
	06	2·6	2·6
	07*	1·1	1·9
	08	5·7	6·3
	09	19·8	−21·5
	10	7·2	−8·5
	11	2·0	2·8
	12*	1·0	−1·0
02	01	24·5	−24·6
	02	20·2	19·5
	03	20·4	−19·3
	04	2·6	2·9
	05	24·8	−21·9
	06	8·9	−8·7
	07	3·4	−1·7
	08*	1·1	1·6
	09*	1·1	1·9
	10	7·1	−7·9
	11	2·0	2·8
	12*	1·1	−1·7
03	01*	0·8	0·8
	02	21·8	20·8
	03	7·3	−5·4
	04	37·6	−33·5
	05	16·6	14·6
	06	8·7	7·8
	07	3·5	2·7
	08*	0·4	0·4
	09*	1·1	1·8
	10	2·5	−2·9
	11	2·0	−2·5
04	01*	0·6	−0·6
	02	17·9	16·8
	03	6·6	6·3
	04	6·4	−5·6
	05	5·9	−4·0
	06	5·9	−6·4
	07	3·6	−1·9
	08	4·6	−3·9
04	09	4·1	−3·8
	10	4·9	−5·6
	11*	0·6	0·6
05	01	2·5	−0·2
	02	6·0	−7·6
	03	8·5	9·0
	04	26·0	−25·6
	05	6·3	−5·2
	06	6·1	−5·5
	07*	1·0	1·4
	08	6·4	−7·6
	09	3·1	−3·4
	10	6·5	−7·7
	11*	0·2	0·2
06	01	7·7	8·2
	02	7·9	−7·4
	03*	0·5	0·5
	04	3·1	−2·9
	05	8·3	−8·9
	06	9·8	11·2
	07*	1·1	1·4
	08*	1·1	2·4
	09	4·2	−4·7
	10	2·0	−2·3
	11*	0·7	−0·7
07	01	2·2	3·8
	02	4·1	−4·0
	03	10·1	−10·1
	04	2·9	4·0
	05	9·4	8·0
	06	9·1	9·1
	07	5·4	−4·5
	08	4·0	−2·7
	09	6·6	−8·1
	10*	0·8	0·8
08	01	4·4	3·3
	02*	0·5	0·5
	03	19·2	18·9
	04	4·4	−2·9
	05	17·4	−18·3
	06	3·3	3·2
	07	5·3	4·7
	08	2·5	2·5
	09	0·5	−0·5
	10*	0·5	−0·5
09	01*	1·1	−2·4
	02	6·9	7·0
	03	17·7	−17·8
	04	9·5	−8·6
	05	16·3	17·6
	06*	1·0	1·0
	07*	1·1	−1·4
	08*	0·6	−0·6
	09*	0·0	0·0
10	01	5·4	5·2
	02	13·7	12·0
	03	8·3	−7·9
	04	5·4	−6·4
	05	7·3	−7·1
	06	6·0	−6·2
	07*	1·2	1·2
	08*	1·2	1·2
	09*	0·0	0·0
11	01	5·4	−5·1
11	02*	1·1	−1·8
	03	3·2	−2·7
	04	12·8	−11·9
	05*	1·1	2·5
	06*	1·1	−2·8
	07*	1·1	1·8
	08	2·3	2·1
12	01*	0·6	0·6
	02	3·5	2·9
	03	1·1	2·7
	04	2·9	3·7
	05*	0·9	0·9
	06*	0·4	0·4
	07	2·4	−2·5
13	01*	1·1	1·7
	02	4·4	−4·0
	03	3·0	−2·2
	04*	1·0	1·4
	05*	0·6	0·6
	06	4·4	−5·4
14	01	2·2	1·3
	02	4·9	−4·8
	03	3·2	−3·6
	04*	0·4	−0·4
15	01*	1·1	−2·2
$h=2$			
00	00	11·2	−8·6
	01*	0·0	0·0
	02	56·0	60·1
	03*	0·0	0·0
	04	3·3	−3·3
	05*	0·0	0·0
	06	6·3	−7·5
	07*	0·0	0·0
	08*	1·1	−1·4
	09*	0·0	0·0
01	00	18·3	−17·9
	01	3·4	1·8
	02	17·8	16·3
	03	1·7	1·4
	04	0·7	0·7
	05	4·1	4·2
	06	2·1	4·7
	07	2·8	−1·9
	08*	0·9	0·9
	09*	0·5	−0·5
02	00	3·7	−2·3
	01	18·5	19·0
	02	23·6	20·2
	03	11·5	−12·9
	04*	1·1	−1·4
	05	5·2	−7·7
	06	3·6	−3·9
	07	4·2	3·7
	08	1·1	2·3
03	00	11·0	−10·0
	01	30·6	35·0
	02	10·0	9·2
	03	2·7	0·0
	04	2·9	2·9
	05	2·9	1·3
	06*	1·2	1·2
	07*	1·1	−3·1
03	08	2·4	2·9
04	00*	1·1	1·9
	01	8·6	−8·4
	02*	1·1	−2·4
	03	8·6	9·0
	04*	0·9	0·9
	05	2·1	1·3
	06*	1·0	1·0
	07	7·1	8·7
	08*	1·1	1·6
05	00	5·7	5·8
	01	10·5	8·9
	02	3·7	−3·6
	03	4·4	3·4
	04*	1·1	−2·8
	05	4·2	−4·0
	06	3·4	1·2
	07	2·3	3·0
	08*	0·5	0·5
06	00*	1·0	1·0
	01	10·6	−9·9
	02	14·1	15·3
	03	9·8	10·2
	04*	1·1	2·9
	05	4·1	6·0
	06	3·7	−4·1
	07	3·0	2·9
	08*	1·1	−1·3
07	00	3·3	2·4
	01	5·5	−7·4
	02	6·9	5·8
	03*	0·1	0·1
	04	5·2	−5·0
	05*	1·1	−1·3
	06	8·5	9·9
	07*	0·4	0·4
08	00*	0·5	−0·5
	01*	0·8	0·8
	02	7·0	7·2
	03*	0·7	0·7
	04	3·5	3·4
	05*	1·1	−2·5
	06	7·0	−8·8
	07	1·8	1·0
09	00	5·2	4·6
	01*	0·2	−0·2
	02	4·8	4·4
	03	2·0	−1·6
	04	1·9	−0·8
	05	3·3	3·8
	06	3·3	4·3
10	00	4·2	−5·1
	01	2·9	2·5
	02	1·1	−2·1
	03*	0·4	0·4
	04	1·6	−2·4
	05*	1·1	−1·4
11	00	2·9	3·0
	01	4·8	−4·4
	02*	0·1	−0·1
	03*	1·1	−1·1
	04*	0·9	−0·9
	05*	0·0	0·0

Table 1 (*cont.*)

kk	*ll*	F_o	F_c
12	00*	0·9	−0·9
	01	3·7	3·4
	02*	1·2	−1·2
	03	3·4	−2·5
	04*	0·7	−0·7
13	00*	0·0	0·0
	01	2·9	−3·8
	02*	0·3	−0·3
14	00*	0·4	−0·4
	01*	0·0	0·0
$h=-2$			
00	01*	0·0	0·0
	02	1·0	1·0
	03*	0·0	0·0
	04	14·6	14·1
	05*	0·0	0·0
	06*	0·2	−0·2
	07*	0·0	0·0
	08	36·1	−33·0
	09*	0·0	0·0
	10	5·4	5·2
	11*	0·0	0·0
	12*	0·7	0·7
01	01	6·1	5·5
	02	8·6	−9·3
	03	8·8	7·8
	04	19·2	−21·4
	05*	0·5	0·5
	06*	0·5	0·5
	07	10·7	10·0
	08	2·0	−1·8
	09	10·5	−9·1
	10	5·4	4·6
	11	2·6	−1·8
	12*	0·8	0·8
02	01	11·4	12·3
	02	7·7	−7·6
	03	12·9	−9·9
	04	19·4	19·6
	05	12·6	9·8
	06	2·3	1·7
	07	10·0	8·0
	08	9·9	−8·0
	09	14·2	−13·1
	10*	1·1	−1·4
	11	3·4	−2·4
	12*	0·1	0·1
03	01	14·5	15·8
	02	7·7	−6·9
	03	1·7	1·3
	04	13·1	−11·8
	05	12·5	−12·3
	06	5·0	−3·1
	07	1·9	−0·7
	08	2·9	−2·9
	09	16·2	−13·4
	10	2·9	2·9
	11	1·1	−1·3
	12*	0·9	−0·9
04	01	7·1	5·1
	02	2·9	3·3
	03	29·0	−31·5
	04	2·1	2·3
	05*	0·5	−1·3
04	06	4·9	4·8
	07	4·4	−5·7
	08	4·8	4·5
	09	5·2	4·5
	10	1·9	−2·5
	11	2·8	−2·2
	12	1·1	−2·9
05	01	4·3	3·6
	02	10·4	10·2
	03	11·4	−9·1
	04	5·2	−3·4
	05	5·3	8·7
	06*	0·3	−0·3
	07	2·0	−0·7
	08	5·9	−5·1
	09	6·2	−5·2
	10*	1·1	−1·5
	11	2·6	−0·9
06	01	3·8	−4·0
	02	4·4	4·8
	03	7·7	−6·2
	04*	0·1	−0·1
	05	11·8	−14·0
	06	5·4	−3·8
	07	7·7	−6·4
	08	10·9	−9·7
	09	6·3	5·8
	10	2·4	1·4
	11*	0·5	0·5
07	01	5·0	−5·0
	02	7·0	−6·1
	03	4·2	−3·3
	04	20·5	−20·7
	05	18·0	17·2
	06	5·9	5·3
	07	3·6	3·0
	08	4·1	−4·5
	09*	0·3	−0·3
	10*	0·0	0·0
	11*	0·4	−0·4
08	01*	1·1	2·2
	02	15·3	−13·1
	03*	1·1	2·0
	04	20·2	16·6
	05	2·6	−2·7
	06	6·6	−5·8
	07	2·0	−1·3
	08	6·8	−5·1
	09	3·4	−2·8
	10*	0·7	0·7
09	01	6·6	6·7
	02	16·0	−14·7
	03	4·8	−3·7
	04	14·2	−12·0
	05	4·2	−4·3
	06	2·9	2·8
	07	2·9	1·5
	08*	1·0	−1·0
	09*	0·2	−0·2
	10*	1·1	−1·8
10	01	2·9	2·8
	02	11·3	−9·8
	03	16·6	−12·7
	04	9·1	8·2
	05	5·1	9·0
10	06	3·3	2·6
	07*	0·1	0·1
	08*	1·1	1·4
	09*	1·1	−1·1
11	01	10·0	9·9
	02	2·0	−1·0
	03	10·6	−8·9
	04*	0·8	0·8
	05*	1·1	−1·5
	06	3·4	−1·7
	07*	1·2	1·2
	08	4·2	−5·0
12	01	1·8	−2·3
	02*	0·9	−0·9
	03	4·9	−5·2
	04	1·1	−1·1
	05	8·2	−7·0
	06*	0·6	−0·6
	07*	1·1	3·5
13	01	3·0	−2·9
	02	1·1	1·1
	03	3·0	−2·8
	04*	0·7	−0·7
	05	3·4	3·3
	06*	1·1	−2·0
14	01*	0·7	0·7
	02	2·0	−1·7
	03	2·1	2·4
	04*	1·1	2·0
$h=3$			
00	00	3·4	1·7
	01*	0·0	0·0
	02*	0·0	0·0
	03*	0·0	0·0
	04*	1·2	1·2
	05*	0·0	0·0
	06*	0·9	2·0
	07*	0·0	0·0
01	00	2·0	2·6
	01	2·3	−1·6
	02	3·6	5·2
	03	15·8	18·7
	04*	0·9	−3·8
	05*	0·3	−0·3
	06*	0·9	−2·8
	07	3·1	−3·7
02	00	3·1	3·5
	01	9·2	−10·7
	02	12·1	13·3
	03	8·1	11·8
	04*	0·9	−2·5
	05*	0·5	0·5
	06*	0·9	2·6
	07*	0·9	1·7
03	00	4·5	4·5
	01*	0·9	−1·8
	02	2·7	3·3
	03	5·1	2·0
	04*	1·2	−1·2
	05*	1·0	−1·0
	06*	0·9	−1·5
04	00	4·3	5·9
04	01*	1·0	1·0
	02	12·7	15·1
	03*	0·3	−0·3
	04*	1·0	−1·0
	05*	0·2	0·2
	06*	1·1	−1·1
05	00	2·5	1·3
	01*	0·6	0·6
	02	2·9	−4·1
	03	2·9	3·4
	04	3·9	5·1
	05*	0·7	0·7
	06*	0·9	3·3
06	00*	0·8	−0·8
	01*	0·9	2·3
	02*	0·9	−2·6
	03*	0·9	0·9
	04	2·5	1·7
	05*	0·9	−3·1
	06*	0·9	−2·3
07	00*	0·0	0·0
	01*	0·5	−0·5
	02*	0·9	−1·5
	03	4·5	6·4
	04*	0·9	2·4
	05*	0·9	2·4
08	00*	0·4	−0·4
	01*	0·9	1·4
	02*	0·9	−2·0
	03	4·3	5·2
	04*	0·7	−0·7
	05*	0·9	−1·5
09	00*	0·9	1·4
	01*	0·9	−3·2
	02*	0·9	1·6
	03	1·1	1·1
	04*	0·3	0·3
10	00	5·8	7·2
	01*	0·9	3·4
	02*	0·9	−0·9
	03*	1·0	1·0
11	00*	0·5	0·5
	01*	0·9	2·0
	02*	0·9	2·2
12	00	2·9	2·3
	01*	0·2	0·2
$h=-3$			
00	01*	0·0	0·0
	02	3·5	3·5
	03*	0·0	0·0
	04	5·4	5·5
	05*	0·0	0·0
	06	10·6	9·3
	07*	0·0	0·0
	08	4·9	3·7
	09*	0·0	0·0
	10*	0·9	−2·1
	11*	0·0	0·0
	12*	0·8	0·8
01	01*	0·4	0·4
	02	2·7	0·6

Table 1 (*cont.*)

kk	*ll*	F_o	F_c
01	03	20·5	15·1
	04	8·3	6·6
	05*	0·9	−2·0
	06	6·0	6·3
	07	21·1	−20·3
	08	13·3	−10·2
	09*	0·9	1·6
	10*	0·9	−0·9
	11*	0·4	0·4
	12*	0·1	0·1
02	01	3·6	−5·7
	02	5·5	6·4
	03	19·8	−14·6
	04	8·4	−6·9
	05	4·1	−5·0
	06	5·8	6·5
	07	6·4	−6·6
	08	15·6	−13·9
	09	7·0	7·1
	10*	0·5	−0·5
	11*	0·6	0·6
	12*	0·1	0·1
03	01	2·9	−3·1
	02	15·2	−11·9
	03	7·9	7·6
	04	4·1	3·9
	05	3·1	4·7
	06	3·5	2·2
	07	4·8	4·5
	08	7·0	6·4
	09	2·9	−3·4
	10*	0·9	−2·5
	11	1·2	−1·2
	12*	0·9	3·0
04	01*	0·9	2·5
	02	6·1	−4·4
	03*	0·4	−0·4
	04	2·2	0·8
	05*	0·9	−2·4
	06*	0·0	0·0
	07	4·1	−2·9
	08	13·6	−12·4
	09	1·2	−1·2
	10	1·1	−1·1
	11*	0·9	−2·5
	12*	0·9	2·1
05	01	4·3	4·6
	02	14·4	−12·4
	03*	0·9	−0·9
	04	12·5	−11·3
	05	3·6	0·6
	06	3·6	−6·0
	07*	0·9	−1·7
	08	5·8	6·2
	09*	0·4	−0·4
	10*	0·5	−0·5
	11*	0·9	−2·9
06	01	3·9	4·9
	02	9·0	−7·2
	03	13·9	−11·5
	04	14·1	12·7
	05	6·1	3·9
	06*	0·7	0·7
	07	4·1	−4·3
	08*	0·4	−0·4
	09*	0·9	−1·3
06	10	3·3	1·9
	11*	0·9	−2·5
07	01*	0·5	−0·5
	02*	0·9	2·0
	03	8·9	7·5
	04	7·9	−7·4
	05	4·9	−6·6
	06*	0·9	−2·4
	07	7·6	−8·3
	08*	0·2	−0·2
	09*	0·9	1·6
	10	3·5	−0·8
	11	1·2	1·2
08	01	5·8	−6·7
	02*	0·5	−0·5
	03	16·0	−14·9
	04*	0·7	0·7
	05*	0·9	4·1
	06*	0·9	2·1
	07	4·8	−4·1
	08	3·6	−0·4
	09*	0·1	−0·1
	10	3·3	−0·3
09	01	7·0	−8·2
	02	5·1	−3·3
	03	8·6	9·1
	04*	0·9	1·7
	05*	0·4	−0·4
	06*	0·7	−0·7
	07*	0·8	−0·8
	08*	0·9	−3·0
	09*	0·9	2·2
10	01	6·0	−6·4
	02	6·1	−5·8
	03*	0·6	−0·6
	04*	0·9	−2·3
	05	1·1	−1·1
	06*	0·2	0·2
	07*	0·6	−0·6
	08*	0·4	0·4
	09*	0·9	−2·8
11	01	3·4	−3·4
	02	6·6	−7·4
	03*	0·3	0·3
	04	4·1	−3·4
	05*	0·9	2·3
	06*	0·9	1·5
	07*	0·7	0·7
	08*	0·8	0·8
12	01*	0·9	1·8
	02	6·8	−6·1
	03*	0·3	0·3
	04*	0·9	2·4
	05	1·2	−1·2
	06*	0·9	1·3
$h=4$			
00	00*	1·1	1·5
	01*	0·0	0·0
	02*	0·1	0·1
	03*	0·0	0·0
	04	9·2	9·9
01	00*	1·0	−1·0
	01*	0·9	0·9
01	02	4·9	−5·6
	03	1·2	1·2
	04	5·5	6·4
02	00	1·2	1·2
	01	3·8	1·6
	02*	1·1	1·4
	03*	1·1	2·5
	04	4·9	5·6
03	00*	1·1	−1·3
	01*	1·1	1·5
	02	3·1	−3·3
	03	11·0	12·6
	04	4·1	4·5
04	00*	0·4	−0·4
	01	2·2	1·8
	02*	1·1	−1·1
	03*	1·1	1·1
	04*	1·1	1·1
05	00	2·2	3·8
	01*	1·1	1·9
	02	4·4	2·5
	03*	1·1	3·8
	04*	1·1	−1·3
06	00*	1·1	3·2
	01	1·2	1·2
	02*	0·0	0·0
	03*	1·0	−1·0
07	00*	1·0	1·0
	01*	1·0	−1·0
	02	4·0	4·7
	03*	1·1	−2·9
08	00	2·7	−1·9
	01*	0·4	0·4
	02*	1·1	−2·3
09	00	5·0	−6·0
	01*	1·1	2·7
10	00	4·1	−5·0
$h=-4$			
00	01*	0·0	0·0
	02	11·9	13·3
	03*	0·0	0·0
	04	4·2	−4·8
	05*	0·0	0·0
	06	15·2	−18·4
	07*	0·0	0·0
	08*	0·7	0·7
	09*	0·0	0·0
	10*	0·2	0·2
	11*	0·0	0·0
01	01	4·1	3·1
	02	5·6	−7·1
	03*	0·8	0·8
	04*	0·7	0·7
	05	6·0	6·8
	06	7·3	−7·2
	07	8·1	−5·5
	08	8·7	7·4
	09*	1·1	−1·4
	10*	0·5	0·5
	11*	1·0	−1·0
02	01	5·3	−5·9
	02	10·4	8·1
	03	5·6	6·3
	04*	1·0	1·4
	05	5·4	5·1
	06	6·5	−4·1
	07	9·9	−10·9
	08*	1·1	−1·6
	09	3·1	−1·8
	10*	0·1	−0·1
	11	2·3	1·0
03	01*	1·1	1·8
	02	4·2	−2·9
	03	2·5	−2·6
	04*	1·1	−2·3
	05	4·8	4·8
	06	7·1	−5·5
	07	14·1	−18·3
	08	4·5	3·4
	09*	0·3	0·3
	10*	0·5	−0·5
	11	2·2	1·3
04	01	9·6	−7·7
	02	2·0	1·5
	03	7·4	−5·7
	04	2·6	3·6
	05*	1·1	−1·1
	06	4·3	4·5
	07*	0·6	−0·6
	08	2·2	−2·5
	09*	1·1	−1·3
	10	3·7	−2·7
	11	4·4	3·4
05	01	8·4	4·2
	02	6·7	−3·3
	03	13·5	9·3
	04	1·2	1·2
	05*	0·0	0·0
	06	2·2	−1·1
	07	6·6	−6·1
	08	4·8	−4·0
	09	2·9	−1·3
	10	5·6	−4·5
	11	2·5	3·4
06	01	3·2	−2·6
	02	4·4	3·0
	03	12·5	−9·9
	04	4·8	−4·3
	05	3·8	−3·0
	06	5·8	−5·6
	07*	1·1	2·7
	08*	0·6	0·6
	09*	0·5	−0·5
	10	2·6	−2·2
07	01	3·1	−2·9
	02	15·2	−13·6
	03	6·2	5·6
	04	5·4	5·3
	05	3·7	1·1
	06	6·5	−5·4
	07*	1·1	1·6
	08*	0·0	0·0
	09*	0·3	0·3
	10*	1·1	−1·3
08	01*	1·1	1·1

Table 1 (*cont.*)

kk	*ll*	F_o	F_c
08	02	5·9	6·4
	03*	0·4	−0·4
	04	3·1	−3·5
	05	5·9	−3·2
	06	6·1	−4·8
	07	4·3	−3·1
	08	2·4	3·0
	09*	1·1	−2·7
09	01	1·8	−1·3
	02	4·3	4·5
	03*	1·1	−2·5
	04*	0·3	−0·3
	05	3·9	1·1
	06	4·1	−2·9
	07*	1·1	−1·3
09	08	3·4	−2·1
10	01	3·8	−4·2
	02	1·6	2·3
	03*	0·8	−0·8
	04	2·9	2·8
	05*	0·3	0·3
10	06*	0·2	0·2
	07	2·5	−2·8
11	02*	1·1	1·8
	03*	1·1	2·0
	04*	1·1	−1·4
	05*	0·4	−0·4

Distances	Length
1–8″	4·177 Å
2–5″	4·844
7–4″	4·386
6–3″	4·230
1–8′	4·644
1–5′	4·576
1–6′	3·659

(Numbering system is shown on Fig. 4).

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The Crystal Structure of *cis* D,L 11-12 Methylene Octadecanoic Acid

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The crystal structure has been determined by two-dimensional Fourier synthesis of the (*h*0*l*) and (0*kl*) diffraction data. In contrast to the 'straight-chain' stereochemistry found in the previously studied C_{19} *trans* cyclopropane acid, this molecule is bent at the *cis* substituted ring so as to have an overall shape somewhat like that of a boomerang.

This compound is believed to be the racemate of the naturally occurring *lactobacillic acid* and is analogous to *dihydrosterculic acid,* in which the *cis* ring is in the 9–10 position.

Introduction

Six *cyclo*propyl fatty acids are at present known; the *cis* and *trans* D,L 9-10, *cis* and *trans* D,L 11-12, methylene octadecanoic acid, which were synthesized by Hofmann *et al.* (1954, 1957); the natural product, *lactobacillic* acid, which was isolated by Hofmann & Lucas (1950) and is believed to be *cis* D or L 11-12, methylene octadecanoic acid from the work of Hofmann, Marco & Jeffrey (1958); the *dihydrosterculic* acid, which is the hydrogenation product of the naturally occurring sterculic acid, $C_{19}H_{34}O_2$, (Nunn, 1952) and was shown by X-ray data to be identical with the *cis* D,L 9-10, methylene octadecanoic acid by Brotherton & Jeffrey (1957); the *dihydromalvalic acid*, which is a hydrogenation product of the naturally