results in an intricate hydrogen-bonding system unique among the reported structures of cyclodiene analogues. The hydrogen bonds, involving intermolecular O—H···O distances ranging from 2·451 to 2·703 Å, form a spiral of molecules down the fourfold screw axes (Fig. 2). The O(10)—HO(10)···O(10′) angle is 170·40° while the HO(10)···O(10′) distance is 1·860 Å. The molecules radiating out from the 4_1 or 4_3 axes at $\frac{1}{4},0,z$; $\frac{1}{4},\frac{1}{2},z$; $\frac{3}{4},0,z$; and $\frac{3}{4},\frac{1}{2},z$ interlock with other molecules such that substituted Cl atoms from different molecules are kept apart. They are arranged in distorted tetrahedra (interatomic distances 2·58 and 3·90 Å) around $\bar{4}$ at $0,\frac{1}{4},\frac{1}{8}$; $0,\frac{3}{4},\frac{7}{8}$; $\frac{1}{2},\frac{3}{4},\frac{5}{8}$; $\frac{1}{2},\frac{1}{4},\frac{3}{8}$. There are also centres of inversion at 0,0,0; $0,\frac{1}{2},0$; $\frac{1}{4},\frac{1}{4},\frac{1}{4}$; $\frac{3}{4},\frac{1}{4},\frac{1}{4}$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$; $\frac{1}{2},0,\frac{1}{2}$; $\frac{3}{4},\frac{3}{4},\frac{3}{4}$; and $\frac{1}{4},\frac{3}{4},\frac{3}{4}$.

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2-Naphthyloxyacetic Acid

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Abstract. $C_{12}H_{10}O_3$, $M_r = 202$, monoclinic, $P2_1/c$, $a = 12{\cdot}298\,(5)$, $b = 6{\cdot}830\,(3)$, $c = 13{\cdot}407\,(7)$ Å, $\beta = 118{\cdot}590\,(8)°$, $V = 988{\cdot}8$ Å^3, $Z = 4$, $D_m = 1{\cdot}37\,(1)$, $D_c = 1{\cdot}356$ g cm^{-3}. The structure, which was refined to an R of 0·083 for 1623 counter reflections, is stabilized by O—H···O hydrogen bonds and forms a centrosymmetric dimer.

Introduction. The study of 2-naphthyloxyacetic acid (BNAA) forms part of a project on structure and function of plant growth hormones. BNAA, a synthetic auxin, has two effects on growth, one relating to cell elongation and the other to the rate of cell division. Auxins possess a naphthalene or benzene group and a side chain of two or more methylene C atoms. Information regarding the orientation of the side chain with respect to the naphthalene group is of interest.

Pink transparent parallelepipeds were obtained from a solution in ethanol. The space group was determined from systematic absences observed on Weissenberg photographs. Cell parameters were obtained by a least-squares fit of 25 θ values measured on a four-circle Picker diffractometer with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54178$ Å). Intensities of 1623 reflections with $2\theta \leq 130°$ were collected with a crystal mounted about b, Ni-filtered Cu $K\alpha$ radiation, a θ–2θ scan, and a 2° min^{-1} scan speed. The scan range was 2° and background was measured on either side of the peak for 10 s. 60 reflections had $I < 2\sigma(I)$ and were excluded. The data were corrected for Lorentz and polarization factors but not for absorption.

The structure was solved with *MULTAN* (Main, Woolfson & Germain, 1971). Improved $|E|$ values were calculated by correcting for molecular scattering with the Debye (1915) formula for the naphthalene group. The E map computed with a set of phases having the fourth highest figure of merit (1·988) revealed the positions of eight atoms, the remaining

Table 1. *Positional parameters*

	x	y	z
C(1)	0·4467 (4)	0·7624 (6)	0·0355 (4)
C(2)	0·4013 (4)	0·5776 (6)	0·0666 (3)
C(3)	0·2685 (4)	0·3082 (6)	−0·0241 (3)
C(4)	0·1835 (4)	0·2211 (7)	−0·1286 (3)
C(5)	0·1232 (3)	0·0542 (6)	−0·1302 (3)
C(6)	0·1452 (4)	−0·0381 (6)	−0·0271 (3)
C(7)	0·0855 (4)	−0·2130 (7)	−0·0249 (4)
C(8)	0·1075 (5)	−0·2953 (8)	0·0765 (4)
C(9)	0·1917 (4)	−0·2069 (7)	0·1796 (4)
C(10)	0·2520 (4)	−0·0394 (6)	0·1806 (3)
C(11)	0·2301 (4)	0·0506 (6)	0·0774 (3)
C(12)	0·2919 (4)	0·2250 (6)	0·0775 (3)
O(1)	0·3243 (3)	0·4759 (4)	−0·0348 (2)
O(2)	0·5195 (3)	0·8635 (4)	0·1251 (2)
O(3)	0·4178 (3)	0·8072 (4)	−0·0615 (2)

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[*] Contribution No. 495.

atoms were retrieved from a difference Fourier synthesis. Block-diagonal least-squares refinement (Shiono, 1968) with unit weights, scale factor and anisotropic temperature factors for all non-hydrogen atoms reduced *R* from 0·54 to 0·10. All ten H atoms were located from a difference Fourier map and included in the structure factor calculation only. The final two cycles of full-matrix refinement were performed with *LALS* (Gantzel, Sparks & Trueblood, 1961); the final *R* was 0·083.

The scattering factors for C, O and H were those given in *International Tables for X-ray Crystallography* (1962). The parameters of the non-hydrogen atoms are listed in Table 1.*

Discussion. Bond lengths and angles are shown in Fig. 1. The average C–C bond length in the naphthalene group is 1·397 (6) Å and the average bond angle is 120·2 (4)°.

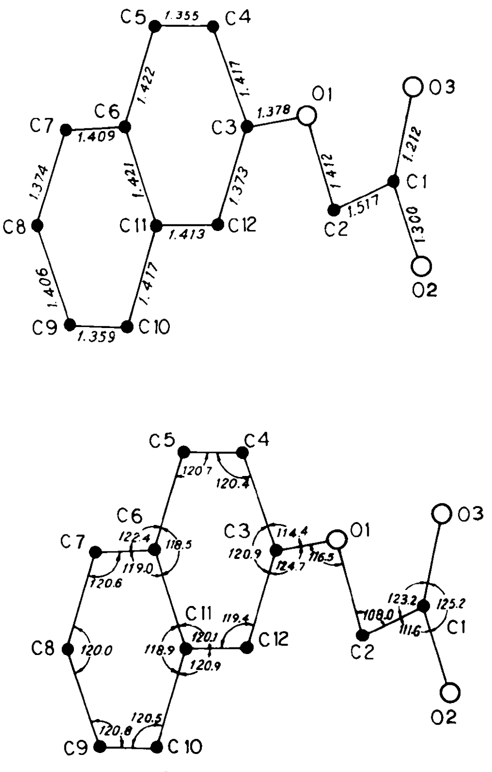

Fig. 1. Bond lengths (Å) and angles (°) in 2-naphthyloxyacetic acid. The e.s.d. of the bond lengths is 0·006 Å and that of bond angles is 0·4°.

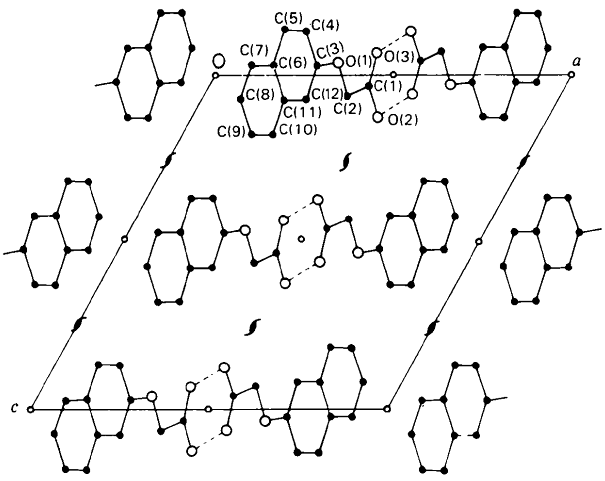

Fig. 2. Packing viewed down *b*.

The carboxyl and the naphthalene groups are planar within experimental error. The deviation of O(1) from the plane through the naphthalene moiety is 0·025 Å. The angle between the carboxyl plane and the naphthalene ring is 4·2° and agrees with that observed in other plant growth hormones, *e.g.* 7·0 and 6·6° for two independent molecules in *o*-chlorophenoxyacetic acid (Chandrasekhar & Pattabhi, 1977) and 5·7° in *trans*-β-2-furylacrylic acid (Filippakis & Schmidt, 1967). This angle is observed to be either close to 0 or to 90° in all plant growth hormones; *e.g.* in 3-indolebutyric acid (Chandrasekhar & Pattabhi, 1978) and 1-naphthaleneacetic acid (Rajan, 1978) it is 93·6 and 98·7° respectively.

The carboxyl group is un-ionized and C(1)=O(3) is *cis* to O(1). The dihedral angle O(3)–C(1)–C(2)–O(1) is 0·4 (5)°. The carboxyl plane is *trans* to the naphthalene group with C(1)–C(2)–O(1)–C(3) = −176·5 (3)°.

Packing down *b* is depicted in Fig. 2. The molecule is stabilized by the O(2)–H···O(3′) hydrogen bond of length 2·649 Å. The distance H···O(3′) is 1·644 Å and relevant angles are C(1)–O(2)···O(3′) = 109·3°, O(2)–H···O(3′) = 166·0° and H–O(2)···O(3′) = 8·6°. As with most plant growth hormones, the molecules form dimers *via* the O–H···O hydrogen bonds.

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3,3′-Dithienyl Ketone

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Abstract. $C_9H_6OS_2$, monoclinic, $P2_1/c$, $a = 6{\cdot}168$ (5), $b = 11{\cdot}168$ (14), $c = 13{\cdot}374$ (35) Å, $\beta = 105{\cdot}33$ (16)°, $M_r = 194{\cdot}3$, $D_x = 1{\cdot}48$ g cm^{-3}. The thiophene rings make angles of 20·9 and 20·1° with the trigonal coordination plane at C(6). The bridging C—C distances of 1·463 (5) and 1·466 (6) Å indicate that there is relatively limited π delocalization between the C=O bond and the thiophene π systems. One of the thiophene rings is disordered.

Introduction. Cell dimensions were obtained from a least-squares fit to the settings for 15 reflexions $\pm(hkl)$ on a Syntex $P2_1$ diffractometer (Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å). Intensity measurements were carried out in the θ–2θ mode ($3{\cdot}5 \leq 2\theta \leq 135{\cdot}0°$) with graphite-monochromated Cu $K\alpha$ radiation at scan speeds varying linearly between 2·93° min^{-1} (150 counts s^{-1} and below) and 29·30° min^{-1} (5000 counts s^{-1} and above). Scan and background times were equal. Lorentz and polarization corrections were applied but no absorption correction [μ(Cu $K\alpha$) = 4·8 cm^{-1}] was made.

After application of the acceptance criterion $I > 2{\cdot}0\sigma(I)$, 1400 unique reflexions were retained for use in the refinement. The structure was solved by direct methods (*SHELX* 76, G. M. Sheldrick) and refined by a blocked full-matrix least-squares method. After introduction of anisotropic temperature factors had led to values for R_G [$= (\sum w\Delta^2/\sum wF_o^2)^{1/2}$] and R of 0·150 and 0·104 respectively, inspection of the difference synthesis revealed electron density peaks of 0·79 e Å^{-3} at 0·47 Å from C(10) and 0·39 e Å^{-3} at 0·45 Å from C(7). These peaks could be best interpreted in terms of a disorder of ring B as depicted in Fig. 1, *i.e.* the ring B' is related to B by rotation of ~180° about the axis C(8)—C(6). The atoms of ring B' were accordingly introduced into the refinement under the following conditions:

(1) The site occupation factors (s.o.f.) of rings B and B' were correlated so that s.o.f. (B') = 1 − s.o.f. (B).

(2) The equivalent distances in the rings B and B' were restrained to refine together with allowed standard deviations in the bond lengths of ±0·01 Å.

(3) The six H atoms of rings A and B were refined with a group isotropic temperature factor under the bond-length constraint that d(C—H) = 1·08 ± 0·01 Å.

(4) The atoms of rings B and B' were at first assigned a joint isotropic temperature factor, then at the final stage of the refinement the former ring atoms were allowed to refine anisotropically. This constrained refinement led, however, to unreasonable values for S(2)—C(10) and S(2′)—C(10′) (1·78 Å).

After inspection of the current values for the S(1)—C(2) and S(1)—C(5) distances in ring A, which should reasonably be similar to those in rings B and B', S(2)—C(7) and S(2)—C(10) and the equivalent bonds in ring B' were constrained to 1·70 ± 0·015 Å. Although this led to a significant increase in R_G (0·086 to 0·094) the

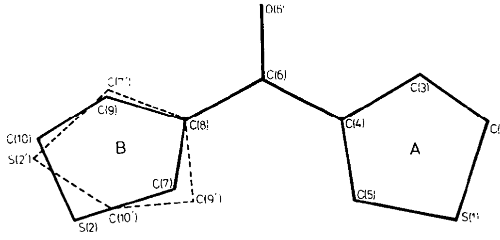

Fig. 1. The B ring disorder in (I).