Table 2. *Table of bond distances* (Å), *bond angles* (°) *and torsion angles* (°)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Br1—C5	2·012 (2)	N3—C4	1·487 (2)
O1—N1	1·249 (2)	C1—C2	1·401 (3)
O2—N1	1·242 (2)	C2—C3	1·501 (3)
O3—N2	1·222 (3)	C4—C5	1·571 (3)
O4—N2	1·230 (3)	C4—C8	1·537 (3)
N1—C1	1·389 (3)	C4—C9	1·528 (3)
N2—C1	1·457 (3)	C5—C6	1·513 (3)
N3—C2	1·316 (3)	C5—C7	1·525 (3)

O1—N1—O2	121·9 (2)	N3—C4—C5	106·7 (2)
O1—N1—C1	118·4 (2)	N3—C4—C8	110·3 (2)
O2—N1—C1	119·6 (2)	N3—C4—C9	109·9 (2)
O3—N2—O4	124·4 (2)	C5—C4—C8	107·9 (2)
O3—N2—C1	117·7 (2)	C5—C4—C9	110·7 (2)
O4—N2—C1	117·9 (2)	C8—C4—C9	111·2 (2)
C2—N3—C4	130·3 (2)	Br1—C5—C4	108·4 (1)
N1—C1—N2	113·1 (2)	Br1—C5—C6	105·1 (2)
N1—C1—C2	126·5 (2)	Br1—C5—C7	105·8 (2)
N2—C1—C2	120·4 (2)	C4—C5—C6	112·7 (2)
N3—C2—C1	120·5 (2)	C4—C5—C7	113·1 (2)
N3—C2—C3	122·0 (2)	C6—C5—C7	111·1 (2)
C1—C2—C3	117·6 (2)		

O1—N1—C1—N2	171·3 (4)	N1—C1—C2—N3	4·0 (3)
O1—N1—C1—C2	−11·4 (4)	N1—C1—C2—C3	−176·3 (3)
O2—N1—C1—N2	−10·7 (3)	N2—C1—C2—N3	−178·9 (3)
O2—N1—C1—C2	166·6 (4)	N2—C1—C2—C3	0·8 (4)
O3—N2—C1—N1	−62·0 (3)	N3—C4—C5—Br1	52·0 (2)
O3—N2—C1—C2	120·6 (3)	N3—C4—C5—C6	167·9 (3)
O4—N2—C1—N1	119·5 (4)	N3—C4—C5—C7	−65·0 (4)
O4—N2—C1—C2	−57·9 (4)	C8—C4—C5—Br1	170·5 (2)
C4—N3—C2—C1	−179·3 (3)	C8—C4—C5—C6	−73·6 (3)
C4—N3—C2—C3	1·0 (3)	C8—C4—C5—C7	53·5 (3)
C2—N3—C4—C5	168·4 (2)	C9—C4—C5—Br1	−67·5 (2)
C2—N3—C4—C8	51·4 (3)	C9—C4—C5—C6	48·4 (3)
C2—N3—C4—C9	−71·6 (2)	C9—C4—C5—C7	175·5 (3)

1·457 (3) Å and to an average value of 1·462 (33) Å for 2236 bond distances between sp^2-hybridized C atoms and nitro-group N atoms extracted from the 1986 release of the Cambridge Structural Database (Allen *et al.*, 1979). Two structures containing the 1,1-dinitroethylene fragment have been solved recently (Gilardi, 1988), both also showing evidence of reduced double-bond character in the C—C bonds.

The molecular structure contains an intramolecular hydrogen bond between H(16) and O(1) with an H(16)···O(1) distance of 2·00 (3) Å and N(3)—H(16)···O(1) angle of 131·9 (9)°. As a result, the O(1)—N(1)—O(2) nitro group is coplanar with an approximate plane defined by the backbone atoms, C(1)—C(2)—N(3)—C(4)—C(5)—C(6).

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Topochemical Studies. XI.* Structures of α-Acetylaminocinnamic Acid Dihydrate, its Photodimer and the Tetrahydrate of the Photodimer

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Abstract. α-Acetylaminocinnamic acid dihydrate (AC2), $C_{11}H_{11}NO_3.2H_2O$, $M_r = 241{\cdot}24$, monoclinic, $P2_1/a$, $a = 18{\cdot}286\ (2)$, $b = 6{\cdot}0823\ (3)$, $c = 11{\cdot}415\ (1)$ Å, $\beta = 105{\cdot}946\ (8)°$, $V = 1220{\cdot}7\ (2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}32\ (1)$, $D_x = 1{\cdot}312$ Mg m^{-3}, $\mu = 0{\cdot}89$ mm^{-1}, $F(000) = 512$, $R = 0{\cdot}047$ for 1936 unique reflections; photodimer, 1,*c*-3-diacetylamino-*t*-2,*c*-4-diphenylcyclobutane-*r*-1,3-dicarboxylic acid tetrahydrate (ACD4), $C_{22}H_{22}N_2O_6.4H_2O$, $M_r = 482{\cdot}48$, monoclinic, $P2_1/a$, $a = 19{\cdot}153\ (2)$, $b = 6{\cdot}0987\ (4)$, $c = 10{\cdot}2964\ (8)$ Å, $\beta = 106{\cdot}424\ (7)°$, $V = 1153{\cdot}6\ (2)$ Å^3, Z

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* Part X: Kashino, Oka & Haisa (1989).

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Table 1. *Experimental details*

	AC2	ACD4	ACD
M.p. (K)	465–467	Above 573	Above 573
Crystal habits	Prismatic *b*	Prismatic *b*	Prismatic *c*
Size of specimen (mm)	0·20 × 0·45 × 0·33	0·13 × 0·40 × 0·21	0·15 × 0·13 × 0·35
Reflections for lattice parameters			
Number	20	20	20
2θ range (°)	20 to 46	28 to 61	17 to 50
Systematic absences	$h0l$ for h odd $0k0$ for k odd	$h0l$ for h odd $0k0$ for k odd	No condition
$2\theta_{\text{max}}$ (°)	125	125	125
Range of h	−20 to 20	−22 to 20	−10 to 9
k	0 to 6	0 to 7	−12 to 12
l	0 to 13	0 to 11	0 to 7
Fluctuation of standard reflections	0·98 to 1·02	0·99 to 1·00	0·98 to 1·01
Number of unique reflections	1936	1829	1671
Number of reflections with $\|F_o\| > \sigma(F_o)$	1885	1809	1608
R_{int}	0·008 for 107 $hk0$ reflections	0·012 for 111 $hk0$ reflections	0·011 for 178 $hk0$ reflections
Number of parameters	215	215	181
Extinction correction g	$7·3 \times 10^{-5}$	$7·3 \times 10^{-6}$	No correction
R	0·047	0·038	0·063
wR	0·058	0·058	0·076
Constants for w			
P	−0·3306	0·0155	−0·0888
q	0·0166	0·0006	0·0086
r	2·9910	3·4278	2·333
S	3·19	1·18	2·63
$\Delta\rho$ max./min. (e Å^{-3})	0·24/−0·21	0·17/−0·16	0·29/−0·25
$(\Delta/\sigma)_{\text{max}}$ for non-H/H	0·04/0·3	0·14/0·3	0·20/0·5

$= 2$, $D_m = 1·38$ (2), $D_x = 1·390$ Mg m^{-3}, $\mu = 0·94$ mm^{-1}, $F(000) = 512$, $R = 0·038$ for 1829 unique reflections; photodimer (ACD), $C_{22}H_{22}N_2O_6$, $M_r = 410·41$, triclinic, $P\bar{1}$, $a = 9·125$ (2), $b = 10·674$ (2), $c = 6·180$ (2) Å, $\alpha = 82·36$ (2), $\beta = 114·79$ (2), $\gamma = 79·65$ (2)°, $V = 522·7$ (2) Å^3, $Z = 1$, $D_m = 1·28$ (1), $D_x = 1·304$ Mg m^{-3}, $\mu = 0·81$ mm^{-1}, $F(000) = 216$, $R = 0·063$ for 1671 unique reflections; Cu $K\alpha$ ($\lambda = 1·54178$ Å), $T = 295$ K. α-Acetylaminocinnamic acid is found to be photodimerizable in the crystals of its dihydrate (AC2). The crystal structures of AC2, the photodimer (ACD) and the tetrahydrate of the dimer (ACD4) have been determined. In the crystals of AC2 the C═C double bonds of the nearest neighbours are related by a $\bar{1}$ with a C···C distance of 3·548 (1) Å. The molecule of the dimer has a $\bar{1}$ symmetry in the crystals of ACD and ACD4, which shows that the photoreaction has topochemically occurred in the crystals of AC2 in spite of the existence of the hydrogen-bond networks.

Introduction. In view of crystal engineering, it is desirable to clarify the effect of hydrogen bonding on crystal structure and solid-state photoreaction. In the present work, it is found that α-acetylaminocinnamic acid dihydrate is photodimerized keeping hydrogen-bond networks in the crystals to form a tetrahydrate of the photodimer.

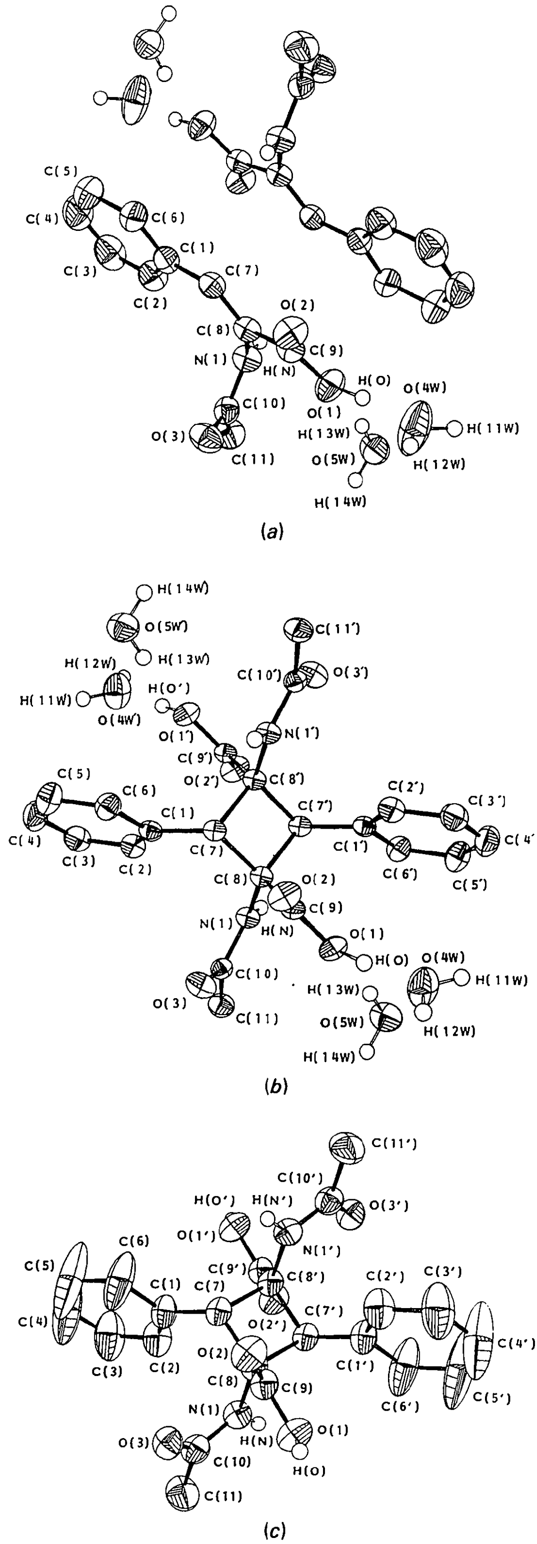
Experimental. Experimental details are listed in Table 1. The crystals of AC2 were grown from an ethanol solution by slow evaporation at 298 K. Photodimerization was effected by exposure of the AC2 crystals to sunlight for a month [the method used by Cohen, Schmidt & Sonntag (1964)]. The crystals of photodimer were prepared from the irradiated sample by vapour diffusion (dimethyl sulfoxide–water system) at 318 K for three weeks. The crystals of ACD4 were grown from the water phase at 298 K and the crystals of ACD from the dimethyl sulfoxide phase at 318 K. For all the crystals D_m was measured by flotation in aqueous KI. Rigaku AFC-5 four-circle diffractometer equipped with rotating anode (Ni-filtered Cu$K\alpha$, at 40 kV, 200 mA); ω–2θ scan method [scan speed 4° min^{-1} in ω for AC2, 6° min^{-1} for ACD4 and ACD, scan range in ω, $(1.2 + 0·15\tan\theta)$° for AC2 and ACD, $(1·2 + 0·20\tan\theta)$° for ACD4], background measured for 4 s on either side of the peak; three standard reflections recorded every 57 reflections. Lorentz and polarization corrections; no absorption correction. All unique reflections within $(\sin\theta/\lambda)_{\text{max}}$ used in structure analyses and refinements. All structures solved by *MULTAN*78 and refined by block-diagonal least-squares method (non-H atoms anisotropically). H atoms determined from difference Fourier maps and refined isotropically; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1·0/[\sigma(F_o)^2 + p|F_o| + q|F_o|^2]$ for $|F_o| > 0$, $w = r$ for $|F_o| = 0$. Correction for secondary extinction with $I_{\text{corr}} = I_o(1 + gI_c)$ applied for the strongest reflections of AC2 and ACD4. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Programs: *RSSFR*-5 (Sakurai, 1967), *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), *HBLS*-V and *DAPH* (Ashida, 1973), *MOLCON* (Fujii, 1979) and *ORTEP* (Johnson, 1971). Computations carried out at the Crystallographic Research Center, Institute for Protein Research, Osaka University, and at the Okayama University Computer Center.

Table 2. *Final atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i \beta_{ii}/a_i^{*2}.$$

	x	y	z	B_{eq}
AC2				
O(1)	0·58817 (6)	0·7251 (2)	0·80715 (9)	3·64 (4)
O(2)	0·53436 (6)	0·9816 (2)	0·67238 (9)	3·67 (5)
O(3)	0·42684 (6)	0·5888 (2)	0·8516 (1)	4·55 (5)
O(4*W*)	0·68941 (7)	0·9919 (2)	0·9190 (2)	6·58 (8)
O(5*W*)	0·65529 (6)	0·3992 (2)	0·9851 (1)	4·25 (5)
N(1)	0·47892 (7)	0·4254 (2)	0·7188 (1)	3·19 (5)
C(1)	0·36982 (8)	0·5400 (2)	0·4640 (1)	3·31 (6)
C(2)	0·34639 (9)	0·3305 (3)	0·4891 (2)	4·15 (7)
C(3)	0·2833 (1)	0·2337 (3)	0·4126 (2)	5·34 (9)
C(4)	0·2418 (1)	0·3416 (3)	0·3092 (2)	5·65 (9)
C(5)	0·2645 (1)	0·5452 (3)	0·2809 (2)	5·24 (8)
C(6)	0·32811 (9)	0·6450 (3)	0·3575 (1)	4·02 (7)
C(7)	0·43288 (7)	0·6664 (2)	0·5423 (1)	3·05 (6)
C(8)	0·47940 (8)	0·6242 (2)	0·6523 (1)	2·89 (5)
C(9)	0·53586 (8)	0·7942 (2)	0·7101 (1)	3·00 (6)
C(10)	0·45176 (8)	0·4206 (2)	0·8164 (1)	3·16 (6)
C(11)	0·4540 (1)	0·2029 (3)	0·8793 (2)	4·60 (8)
ACD4				
O(1)	0·58829 (5)	0·6532 (2)	0·80803 (9)	2·40 (4)
O(2)	0·52934 (6)	0·8995 (2)	0·6565 (1)	2·75 (4)
O(3)	0·42732 (6)	0·5794 (2)	0·8019 (1)	3·16 (4)
O(4*W*)	0·68507 (7)	0·9292 (2)	0·9277 (2)	4·30 (6)
O(5*W*)	0·65861 (7)	0·3427 (2)	1·0171 (1)	3·84 (5)
N(1)	0·48533 (6)	0·3499 (2)	0·6959 (1)	1·99 (4)
C(1)	0·36751 (7)	0·5283 (2)	0·4312 (1)	2·08 (5)
C(2)	0·33976 (8)	0·3238 (2)	0·4510 (1)	2·55 (6)
C(3)	0·26678 (9)	0·2770 (3)	0·3939 (2)	3·14 (6)
C(4)	0·22070 (8)	0·4316 (3)	0·3168 (2)	3·46 (7)
C(5)	0·24790 (9)	0·6350 (3)	0·2957 (2)	3·38 (7)
C(6)	0·32047 (8)	0·6832 (3)	0·3532 (2)	2·64 (6)
C(7)	0·44705 (7)	0·5873 (2)	0·4751 (1)	1·78 (5)
C(8)	0·50349 (7)	0·5141 (2)	0·6094 (1)	1·81 (5)
C(9)	0·53999 (7)	0·7110 (2)	0·6946 (1)	1·98 (5)
C(10)	0·45131 (7)	0·3953 (2)	0·7903 (1)	2·02 (5)
C(11)	0·44827 (8)	0·2094 (3)	0·8842 (1)	2·91 (6)
ACD				
O(1)	0·0998 (2)	0·6135 (2)	0·1269 (2)	4·01 (6)
O(2)	0·2743 (2)	0·5365 (2)	−0·0203 (2)	4·13 (6)
O(3)	0·1788 (2)	0·3183 (2)	0·2813 (3)	4·17 (7)
N(1)	0·2906 (2)	0·4348 (2)	0·5543 (3)	3·62 (7)
C(1)	0·6057 (3)	0·2632 (2)	0·5771 (4)	3·81 (9)
C(2)	0·6085 (3)	0·2104 (2)	0·7977 (4)	4·8 (1)
C(3)	0·6721 (5)	0·0776 (3)	0·9001 (5)	7·3 (2)
C(4)	0·7312 (7)	−0·0032 (3)	0·7904 (7)	11·8 (3)
C(5)	0·7348 (8)	0·0475 (3)	0·5772 (8)	13·3 (3)
C(6)	0·6725 (5)	0·1800 (3)	0·4711 (5)	8·2 (2)
C(7)	0·5402 (2)	0·4070 (2)	0·4542 (3)	3·06 (8)
C(8)	0·3696 (2)	0·4913 (2)	0·4188 (3)	3·13 (8)
C(9)	0·2427 (2)	0·5470 (2)	0·1489 (3)	3·29 (8)
C(10)	0·2015 (3)	0·3494 (2)	0·4771 (4)	3·69 (9)
C(11)	0·1323 (4)	0·2938 (3)	0·6366 (5)	6·7 (2)

Discussion. The final atomic parameters are listed in Table 2.* Thermal ellipsoids of the molecules are shown in Fig. 1, with atomic numbering. Bond lengths and angles are listed in Table 3. Stereoscopic views of the crystal structures are shown in Fig. 2. Geometries of the hydrogen bonds are summarized in Table 4.



(*a*)

(*b*)

(*c*)

Fig. 1. The thermal ellipsoids (50% probability) with atomic numbering. The H atoms attached to the O and N atoms are represented as spheres equivalent to $B = 1{\cdot}0$ Å^2. (*a*) AC2, the molecule related by a $\bar{1}$ is also drawn for the sake of comparison with that of ACD4. For (*b*) ACD4 and (*c*) ACD, the atoms related by a $\bar{1}$ are denoted with a prime.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths and angles involving H atoms, and selected torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52014 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	AC2	ACD4	ACD
O(1)—C(9)	1·318 (1)	1·316 (1)	1·310 (3)
O(2)—C(9)	1·216 (1)	1·213 (1)	1·209 (3)
O(3)—C(10)	1·231 (1)	1·232 (1)	1·240 (3)
N(1)—C(8)	1·429 (1)	1·446 (1)	1·454 (3)
N(1)—C(10)	1·339 (1)	1·343 (1)	1·333 (3)
C(1)—C(2)	1·399 (3)	1·393 (2)	1·392 (4)
C(1)—C(6)	1·399 (3)	1·393 (2)	1·373 (6)
C(1)—C(7)	1·467 (2)	1·505 (1)	1·507 (4)
C(2)—C(3)	1·374 (3)	1·384 (3)	1·380 (6)
C(3)—C(4)	1·381 (3)	1·379 (3)	1·338 (9)
C(4)—C(5)	1·373 (3)	1·386 (3)	1·372 (10)
C(5)—C(6)	1·388 (3)	1·380 (3)	1·380 (9)
C(7)—C(8)	1·334 (1)	1·560 (1)	1·562 (3)
C(8)—C(9)	1·482 (1)	1·534 (1)	1·532 (3)
C(10)—C(11)	1·501 (2)	1·502 (2)	1·491 (4)
C(7)—C(8′)		1·582 (1)	1·574 (3)
O(1)—C(9)—O(2)	122·5 (1)	123·5 (1)	124·7 (2)
O(1)—C(9)—C(8)	114·06 (9)	112·95 (9)	111·2 (2)
O(2)—C(9)—C(8)	123·4 (1)	123·3 (1)	123·9 (2)
O(3)—C(10)—N(1)	120·6 (1)	121·9 (1)	120·7 (2)
O(3)—C(10)—C(11)	122·7 (1)	122·8 (1)	122·3 (2)
N(1)—C(10)—C(11)	116·7 (1)	115·2 (1)	117·0 (2)
N(1)—C(8)—C(9)	117·33 (9)	109·86 (8)	110·2 (2)
C(1)—C(2)—C(3)	120·8 (2)	120·2 (2)	120·3 (3)
C(1)—C(6)—C(5)	120·7 (2)	120·8 (2)	120·5 (5)
C(1)—C(7)—C(8)	131·6 (1)	125·91 (9)	122·5 (2)
C(1)—C(7)—C(8′)		117·00 (8)	120·3 (2)
N(1)—C(8)—C(7′)		110·71 (8)	110·9 (2)
C(2)—C(3)—C(4)	120·5 (2)	120·6 (2)	121·2 (5)
C(3)—C(4)—C(5)	119·9 (2)	119·6 (2)	119·4 (6)
C(4)—C(5)—C(6)	120·1 (2)	120·1 (2)	120·6 (6)
C(6)—C(1)—C(2)	118·0 (2)	118·7 (2)	118·0 (3)
C(6)—C(1)—C(7)	116·1 (2)	116·5 (1)	118·3 (3)
C(7)—C(1)—C(2)	125·9 (2)	124·5 (1)	123·7 (3)
C(7)—C(8)—C(9)	118·09 (9)	111·86 (8)	113·1 (2)
C(7)—C(8)—N(1)	124·57 (9)	121·12 (9)	117·5 (2)
C(8)—N(1)—C(10)	121·21 (9)	123·58 (9)	121·8 (2)
C(7)—C(8)—C(7′)		89·83 (7)	90·1 (2)
(8)—C(7)—C(8′)		90·17 (7)	89·9 (2)
C(9)—C(8)—C(7′)		111·93 (8)	113·9 (2)

The monomer molecules in AC2 are arranged nearly parallel to $(\bar{4}03)$. The molecules related by a *b* translation are held together by N—H···O hydrogen bonds between the carboxyl groups and the amide groups. The molecules related by a $\bar{1}$ at $(0,\frac{1}{2},0)$ are held together by two O—H···O hydrogen bonds through O(5*W*) and the molecules related by a twofold screw axis at $x = \frac{1}{4}$ and $z = 0$ are held together by the other O—H···O hydrogen bonds through O(4*W*) and O(5*W*) between the carboxyl groups and the amide groups. O(4*W*) is linked to O(5*W*) $(x, 1+y, z)$ by an additional O—H···O hydrogen bond. Thus, the two-dimensional hydrogen-bond networks are formed on (001). The crystals are grown along *b*. The C(7)···C(8) distance between the molecules related by a $\bar{1}$ at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ is 3·548 (1) Å, the interplanar spacing being 3·444 (1) Å for the plane through C(1), C(7), C(8) and C(9).

The crystals of ACD4 belong to the same space group as those of AC2 and their cell dimensions are similar. Hydrogen-bond networks in ACD4 are also similar to those in AC2. The similarity in the crystal structures of the monomer and the photodimer is remarkable as found in benzylidenecyclopentanone derivatives and their photodimers (Nakanishi, Jones, Thomas, Hursthouse & Motevalli, 1981; Jones & Theocharis, 1984). The atom movement Δd in the solid-state photoreaction estimated by the method of Nakanishi *et al.* (1981) is largest at C(8), 1·010 Å, and is smallest at C(1), 0·344 Å; $\Delta d = 0{\cdot}539$ Å for O(4*W*) and 0·452 Å for O(5*W*).

The periods of the axes *a*, *b* and *c* in ACD correspond to *c*, $(a+b)/2$ and *b* in ACD4. In the crystals of ACD the molecules related by a *c* translation are held together by intermolecular N—H···O hydrogen bonds between the carboxyl groups and amide groups, and there are additional O—H···O hydrogen bonds between these groups of molecules related by a $\bar{1}$ at $(0,\frac{1}{2},0)$ as found in ACD4. However, in ACD there exist no water molecules which can participate in the hydrogen bonds along a twofold screw axis as in ACD4 and thus the space group descends to $P\bar{1}$ from $P2_1/a$ of ACD4.

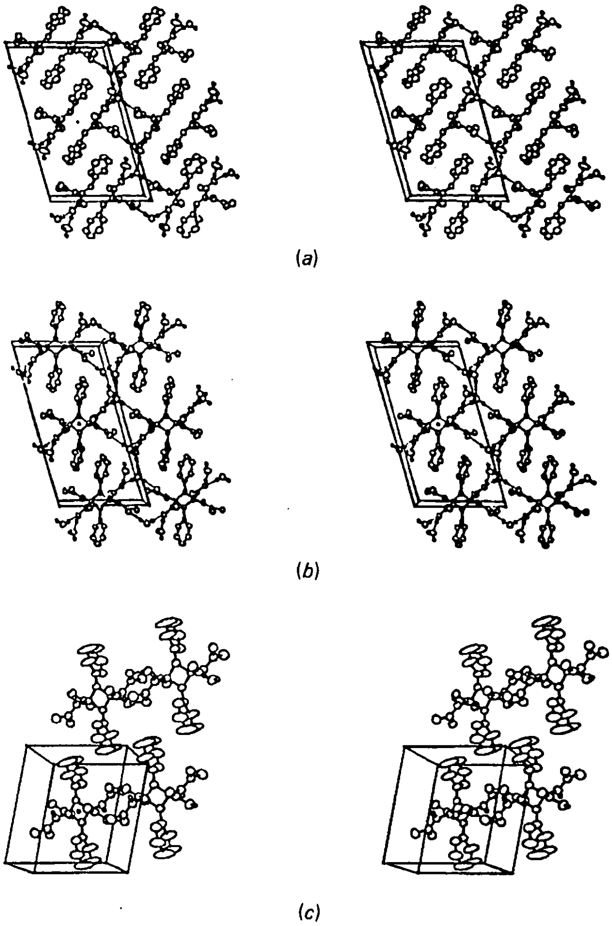

Fig. 2. Stereoscopic views of the molecular packing in the crystals. The H atoms attached to the C atoms are omitted. For (*a*) AC2 and (*b*) ACD4, the *a* axis points upwards, the *b* axis onto the plane of the paper, and the *c* axis from left to right. For (*c*) ACD, the *a* axis points from left to right, the *b* axis upwards, and the *c* axis onto the plane of the paper.

Table 4. *Geometry of hydrogen bonds*

Donor (*D*)	Acceptor (*A*)	*D*···*A* (Å)	H···*A* (Å)	*D*—H···*A* (°)
AC2				
$N(1^{i})$	$O(2^{ii})$	2·982 (1)	2·12 (2)	168 (2)
$O(1^{i})$	$O(4W^{i})$	2·528 (2)	1·53 (2)	170 (2)
$O(5W^{i})$	$O(1^{i})$	2·862 (1)	2·01 (2)	168 (2)
$O(4W^{i})$	$O(5W^{iii})$	2·712 (2)	1·89 (2)	178 (2)
$O(5W^{i})$	$O(3^{iv})$	2·697 (1)	1·84 (2)	172 (2)
$O(4W^{i})$	$O(5W^{v})$	2·806 (2)	1·90 (2)	172 (2)
ACD4				
$N(1^{i})$	$O(2^{ii})$	2·935 (1)	2·05 (2)	174 (2)
$O(1^{i})$	$O(4W^{i})$	2·549 (2)	1·55 (2)	168 (2)
$O(5W^{i})$	$O(1^{i})$	2·897 (1)	2·00 (2)	173 (2)
$O(4W^{i})$	$O(5W^{iii})$	2·780 (2)	1·86 (3)	171 (3)
$O(5W^{i})$	$O(3^{iv})$	2·853 (1)	1·94 (3)	176 (3)
$O(4W^{i})$	$O(5W^{v})$	2·933 (2)	2·09 (3)	171 (3)
ACD				
$N(1^{i})$	$O(2^{ii})$	3·023 (3)	2·11 (2)	175 (2)
$O(1^{i})$	$O(3^{iii})$	2·613 (3)	1·69 (3)	158 (3)

Symmetry code: For AC2 and ACD4 (i) x, y, z; (ii) $x, -1+y, z$; (iii) $x, 1+y, z$; (iv) $1-x, 1-y, 2-z$; (v) $\frac{3}{2}-x, \frac{1}{2}+y, 2-z$. For ACD (i) x, y, z; (ii) $x, y, 1+z$; (iii) $-x, 1-y, -z$.

For the monomer molecule in AC2 the torsion angles C(2)—C(1)—C(7)—C(8), C(1)—C(7)—C(8)—C(9), C(1)—C(7)—C(8)—N(1), C(7)—C(8)—N(1)—C(10) and C(7)—C(8)—C(9)—O(2) are −3·1 (2), −177·0 (1), 3·2 (2), −107·1 (1) and 12·1 (2)°, respectively. This means that the benzene ring, the C=C double bond and the carboxyl group are nearly coplanar, and the amide group is nearly perpendicular to these portions. The length of the C(7)=C(8) bond is typical for cinnamic acids (Glusker, Zacharias & Carrell, 1975). The bond angles C(2)—C(1)—C(7), C(1)—C(7)—C(8) and C(7)—C(8)—N(1) are widened by intramolecular repulsions of C(2)···C(8), 3·176 (2) Å and C(2)···N(1), 3·097 (2) Å, as found in *α*-methylcinnamic acid (Bryan & White, 1982).

The cyclobutane ring in ACD4 has a $\bar{1}$ as expected from the crystal structure of AC2 (the atoms related by the $\bar{1}$ are denoted with a prime hereafter). The conformations of the exocyclic bonds are *cis* for C(1)—C(7)—C(8)—N(1), 10·0 (1)° and *gauche* for C(1)—C(7)—C(8′)—N(1′), 105·3 (1)°. Thus, the photoreaction has topochemically occurred between C(7) and C(8′) in the crystals of AC2 (Kashino, Oka & Haisa, 1989). The angles C(1)—C(7)—C(8) and C(7)—C(8)—N(1) are enlarged by intermolecular repulsions C(3)···C(5) ($\frac{1}{2}-x, \frac{1}{2}+y, 1-z$), 3·399 (3) Å. The C(7)—C(8′) bond is lengthened by intramolecular repulsions C(1)···C(9′), 2·871 (1) Å and C(2)···C(9′), 3·090 (2) Å.

The cyclobutane ring in ACD also has a $\bar{1}$. The torsion angle C(1)—C(7)—C(8)—N(1) is 13·1 (3)° and C(1)—C(7)—C(8′)—N(1′) is 111·9 (2)°. The widening of the angles C(1)—C(7)—C(8) and C(7)—C(8)—N(1) is less than that in ACD4 because of the absence of the intermolecular repulsions. The C(7)—C(8′) bond is lengthened as in ACD4. The thermal vibration of the phenyl ring is enlarged because of the loose packing, the shortest distance being 4·05 (1) Å for C(4)···C(5) ($1-x, -y, 1-z$).

In the photoreactive cinnamic acids which have no additional intermolecular hydrogen bonds other than those between the carboxylic groups, the nearest C···C distances between the C=C bonds are in the range of 3·66 to 4·84 Å (cinnamic acid, Bryan & Freyberg, 1975; *p*-chlorocinnamic acid, Glusker *et al.*, 1975; *p*-methylcinnamic acid, Kashino *et al.*, 1989; *p*-formylcinnamic acid, Nakanishi, Hasegawa & Mori, 1985). In the photoreactive cinnamic acids which have some additional hydrogen bonds the distances are in the range of 3·54 to 3·78 Å (2-hydroxycinnamic acid, Raghunathan & Pattabhi, 1979; 3-hydroxycinnamic acid, Raghunathan & Pattabhi, 1981; 4-hydroxycinnamic acid, Bryan & Forcier, 1980) and in the photostable cinnamic acids which have the additional hydrogen bonds the distances of 4·00 and 4·11 Å are found (3,4-dihydroxycinnamic acid, Granda, Beurskens, Beurskens, Krishna & Desiraju, 1987; cinnamamide, Iwamoto, Kashino & Haisa, 1989). This fact suggests that the intermolecular hydrogen bonds do not necessarily prohibit the solid-state photoreaction, but diminish the photoreactivity when the C···C distance is large (above about 4 Å).

No decrease in weight was observed during the photoreaction of AC2 and a powder photograph of the irradiated crystals was the same as that of ACD4. This indicates that the photoreaction occurs in the solid state keeping the hydrogen bonds involving the water molecules in AC2.

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2-Phenylsparteine

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Abstract. $C_{21}H_{30}N_2$, $M_r = 310{\cdot}48$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}586\,(5)$, $b = 14{\cdot}415\,(2)$, $c = 16{\cdot}936\,(4)$ Å, $V = 1851{\cdot}9\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}12$ g cm^{-3}, m.p. = 352–353 K, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 0·6 cm^{-1}, $F(000) = 680$, $T = 292$ K, final $R = 0{\cdot}044$ for 1489 observed reflections. The quinolizidine moieties both have *trans* configurations, and piperidine rings *A*, *B*, *C* and *D* have chair, chair, boat and chair conformations, respectively. The phenyl subtituent at C(2) is equatorial.

Introduction. This structure determination of 2-phenylsparteine (I) continues our studies on sparteine derivatives (Kałuski, Skolik & Wiewiórowski, 1978; Szymczak, 1983). Our previous X-ray determinations of 2-phenyl derivatives of sparteine included 2-phenylsparteine *N*(16)-oxide monoperchlorate (Małuszyńska & Okaya, 1977), 2-(*p*-tolyl)-2-dehydrosparteine (Małuszyńska, Boczoń & Kałuski, 1986) and $\Delta^{1(2)}$-dehydro-2-phenylsparteine diperchlorate (Boczoń, Kałuski & Małuszyńska, 1987). The synthesis of 2-phenylsparteine has been described and the configuration of C(2), as well as the configuration of the flexible *C*/*D* moiety, have been determined on the basis of a comparison of IR spectra of this compound with those of monodeuterated derivatives (Boczoń, 1981). The sparteine molecule consists of two quinolizidine moieties (rings *A*–*B* and *C*–*D*). The configuration of the quinolizidine moieties is *trans*–*trans* for α-isosparteine, *trans*–*cis* for sparteine and *cis*–*cis* for β-isosparteine (for molecules with all four piperidine rings in chair conformation). The *trans* form is rigid, while the *cis* form is flexible. Thus, in sparteine and β-isosparteine the inversion of N(16), the conversion of ring *C* from chair to boat, and the change of configuration of moiety *C*/*D* from *cis* to *trans* are possible. These compounds, as free bases in the liquid state and in solution, exist predominantly with ring *C* in the boat form (Bohlmann, Schumann & Arndt, 1965; Skolik, Krueger & Wiewiórowski, 1970). The main aim of this X-ray determination was to confirm the spectroscopic results concerning the conformation of ring *C* and to determine the orientation of the phenyl substituent at C(2).

Experimental. Crystals of (I) suitable for X-ray analysis were obtained from ethanol solution. Colourless elongated plates, crystal dimensions 0·3 × 0·3 × 0·2 mm. CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, unit-cell parameters from least-squares fit to 25 reflections ($9{\cdot}9 \leq 2\theta \leq 13{\cdot}7°$), 2θ–θ scan method, variable scan speed (2·0–20·0° min^{-1}) depending on reflection intensity. 1895 reflections up to $2\theta = 50°$ were measured: h 0→9, k 0→17, l 0→6; no systematic variation in intensity was observed for three control reflections measured every 2 h, Lp corrections, no absorption corrections, 1489 reflections with $I \geq 1{\cdot}96\sigma(I)$ were considered observed. The structure was solved by direct methods with *SHELX76* (Sheldrick, 1976) and the absolute configuration of the molecule was assigned according to the previous determination of the absolute configuration of the naturally occurring sparteine derivatives as C(7) *S* and C(9) *S* (Klyne, Scopes, Thomas, Skolik, Gawroński & Wiewiórowski, 1974). The positions of all H atoms were recalculated from the geometry of the molecule after each cycle of refinement, all H atoms were assigned an equal isotropic temperature factor of

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