Fig. 2. *ORTEP* (Johnson, 1965) projections down (i) **b** and (ii) **c**.

in opposite directions. This is the conformation reported for the methoxy groups in 1,4-dimethoxybenzene (Goodwin, Przybylska & Robertson, 1950). The ester groupings form planes normal to the adjacent phenyl ring.

Krigbaum, Watanabe & Ishikawa (1983) have studied the liquid-crystal behaviour of poly(esters) based on 4,4'-dihydroxybiphenyl. The molecules take up extended forms with the ester groups *cis* for an odd number and *trans* for even number of methylene units. This is compatible with the present structure as shown in the figures, where the unit-cell contents are shown in Fig. 2 in projections down **b** and **c**. The approximately linear molecules pack in a parallel manner confirming the potential for liquid-crystal behaviour when acting as side groups on polymer chains. Several short inter-molecular contacts have been observed (Table 2), particularly one of 3·533 (3) Å between the methyl

group, C(1), and the phenyl ring at C(7), and one of 3·446 (5) Å between C(2) and C(3) in adjacent phenyl rings. These intermolecular contacts indicate that interactions between the phenyl rings and the polar groups on neighbouring rings are of prime importance in determining the packing geometry.

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Ammonium Hydrogen Oxalate Hemihydrate: X-ray and Neutron Diffraction Studies

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Abstract. $NH_4^+.HC_2O_4^-.1/2H_2O$, $M_r = 116·1$, ortho-rhombic, *Pnma*, $a = 11·237$ (1), $b = 12·341$ (2), $c = 6·901$ (1) Å, $V = 957·00$ (2) Å^3, $Z = 8$, $D_m = 1·614$, $D_x = 1·612$ Mg m^{-3}, $F(000) = 488$, $T = 295$ K; (1) X-ray data, Mo $K\alpha$, $\lambda = 0·71069$ Å, μ(calc.) = 0·1509 mm^{-1}, 1781 unique reflections, $R = 0·0331$; (2) neutron data, $\lambda = 1·210$ Å, μ(obs.) = 0·2316 mm^{-1}, 2093 reflections measured, $R = 0·0397$. The hydrogen oxalate ions form infinite chains *via* an asymmetric hydrogen bond, with an O$\cdots$O distance of 2·562 (1) Å. Ammonium ions are disordered. The H-atom sites in the ammonium ions have similar possibilities for hydrogen bonding. The shortest separation between disordered sites is 0·22 (5) Å and the largest is 0·90 (1) Å. Both data sets were corrected for thermal diffuse scattering.

Introduction. The present work is part of a project involving studies of the influence of the environment on the electron and proton distribution in acid salt compounds containing hydrogencarbonate or hydro-gen carboxylate groups (Fernandes, Tellgren & Olovsson, 1988).

The X-ray structure of $NH_4HC_2O_4.1/2H_2O$ has been investigated by Küppers (1973). Some physical properties of this compound have been measured by Küppers and co-workers, *e.g.* density (Küppers, 1973),

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Table 1. *Details of the data collection and structure refinement*

	X-ray	Neutron
Diffraction technique		
Diffractometer	Enraf–Nonius CAD-4	Hilger & Watts four circle
Wavelength (Å) and monochromator	0·71069 graphite	1·210 Cu(220) double system
Crystal volume (mm³)	$4·67 \times 10^{-3}$	54·3
Number and θ range of reflections in orientation matrix	25 $10 < \theta < 15°$	25 $10 < \theta < 15°$
Maximum TDS correction (α), where $I(\text{corr.}) = I(\text{obs.})(1+\alpha)$	0·22	0·16
Transmission factor (min., max. values)	0·968, 980	0·447, 0·549
Max. value of $(\sin\theta)/\lambda$ (Å⁻¹)	1·024	0·63
Range of h	0, 22	0, 9
k	0, 24	0, 15
l	0, 11	−15, 17
Number of standard reflections and their variation with time (%)	5 7	5 5
Number of reflections measured, ω–2θ step scan mode	2205	2953
Number of unique reflections	1785	2093*
$R(\text{int})$	0·0117	0·0324
Number of unobserved reflections, $I < 2\sigma(I)$	0	472
$R = \sum\|F_o - F_c\|/\|F_o\|$	0·0309	0·0325†
$R = \sum\|F_o^2 - F_c^2\|/\sum\|F_o^2\|$	0·0649	0·0464†
$w = 1/[\sigma^2(F_o^2) + k^2F_o^4]$, $k =$	0·033	0·022
$wR = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$	0·0853	0·0640†
$S = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$	2·07	1·73†
Ratio of maximum least-squares shift to e.s.d. in final cycle $(\Delta/\sigma)_{max}$	0·01	0·01
Min. and max. heights in difference maps (e Å⁻³) and (nuclei Å⁻³)	−0·19, 0·38	−0·06, 0·09
Maximum extinction correction (y), where $F^2(\text{corr.}) = yF^2(\text{corr.})$	1·77	7·06

* Number of reflections after averaging only those measured more than once due to anisotropic extinction effects.

† Model chosen, see text reference to the neutron data refinements.

Table 2. *Summary of some neutron data refinements based on F^2*

The number of observations is 1621. In the third column p means the number of parameters varied.

Refinement	Model refined	p	R	wR	S
1	Ordered model.	139	0·0579	0·0843	2·25
2	H4 as half atom in general position.	142	0·0519	0·0749	2·00
3	As 2 but H5 refined as two independent 1/2 H. β's of H55 constrained to follow β's of H5 (anisotropic temp. factors).	145	0·0517	0·0735	1·97
4	As 3 but H3 as half atom in general position.	148	0·0514	0·0725	1·94
5	As 3 but β's of H5 and H55 refined independently of each other.	151	0·0493	0·0685	1·84
6	As 5 but H3 as half atom in general position.	154	0·0489	0·0676	1·81
7	As 3 but H7 as half atom in general position and H8 refined as two independent 1/2 H. β's of H88 constrained to follow β's of H8.	151	0·0514	0·0730	1·96
8	As 7 but H6 as half atom in general position.	157	0·0506	0·0717	1·93
9	As 5 but H7 as half atom in general position and β's of H8 and H88 refined independently of each other.	163	0·0475	0·0658	1·77
10*	As 9 but H3 and H6 as half atoms in general position.	169	0·0464	0·0640	1·73

* Model chosen.

elastic constants (Küppers, 1972*b*), directions of dislocation lines in the crystal growth from solution (Klapper & Küppers, 1973), thermal expansion tensors (Küppers, 1974); a phase transition was observed at 145·6 K and an X-ray structural study of the ferroelastic low-temperature phase has been made by Keller, Kucharczyk & Küppers (1982). The present X-ray and neutron diffraction studies at room temperature are the first step to understand the behaviour of ammonium groups and the role of hydrogen bonds in the phase transition.

Experimental. *Crystal growth and cell parameters.* Single crystals of $NH_4HC_2O_4.1/2H_2O$ were grown at room temperature from an aqueous solution obtained by dissolution of equivalent amounts of commercial ammonium oxalate dihydrate, $(NH_4)_2C_2O_4.2H_2O$, and oxalic acid dihydrate, $H_2C_2O_4.2H_2O$, on slow evaporation (Küppers, 1972*a*). The unit-cell parameters were determined from powder photographs taken with a Guinier–Hägg focusing camera, Ni filter, $\lambda(\text{Cu }K\alpha)$ = 1·5418 Å, Si ($a = 5·4309$ Å) used as internal standard, 22 reflections indexed. JCPDS No. 39-1405.

Data collection, TDS correction and data reduction. The neutron data collection was performed at the Swedish Research Reactor, R2, in Studsvik. The flux at the crystal was $\sim 1·3 \times 10^4$ neutrons mm⁻² s⁻¹.

For both data sets: (1) reflection profiles were corrected for background using the Lehmann & Larsen (1974) method; (2) intensities were corrected for thermal diffuse scattering (TDS) using the elastic constants measured by Küppers (1972*b*) and a local version of the computer program written by Stevens (1974); (3) Lorentz (polarization for X-ray data) and absorption corrections were applied. These data are summarized in Table 1. All computer programs used have been described by Lundgren (1982).

X-ray refinement. For non-H atoms the starting parameters were taken from Küppers (1973). Scattering factors and dispersion corrections were from *International Tables for X-ray Crystallography* (1974). H atoms were located from subsequent $\Delta\rho$ maps.

As $Z = 8$ and the multiplicity of the general position is eight, the two N atoms in the asymmetric unit lie on the mirror plane as well as the O atom of the water molecule. With all atoms of the hydrogen oxalate group on general positions, each ammonium group should have two H atoms on the mirror plane and one H atom in a general position. Difference Fourier maps showed

Table 3. *Atomic coordinates and equivalent isotropic thermal parameters* ($\mathring{A}^2$)

The upper row refers to the X-ray data, the second row to the neutron data.

$\langle u^2 \rangle = \frac{1}{3}(\frac{1}{2}\pi^2)\sum_i\sum_j\beta_{ij}(\mathbf{a}_i.\mathbf{a}_j)$, except for the H atoms in the X-ray data.

	x	y	z	$\langle u^2 \rangle \times 10^2$
O1	0·47877 (4)	0·60280 (4)	0·16173 (9)	3·10 (4)
	0·47874 (9)	0·60252 (7)	0·16209 (18)	3·08 (9)
O2	0·41004 (4)	0·44915 (4)	0·29365 (10)	3·46 (4)
	0·41016 (8)	0·44943 (8)	0·29367 (18)	3·36 (10)
O3	0·70036 (4)	0·53026 (4)	0·18756 (11)	3·79 (4)
	0·70029 (8)	0·52974 (8)	0·18748 (21)	3·66 (11)
O4	0·63586 (5)	0·37491 (5)	0·31617 (12)	4·10 (5)
	0·63594 (9)	0·37546 (9)	0·31685 (20)	3·93 (10)
O5	0·20851 (7)	0·25000	0·64862 (15)	3·81 (7)
	0·20820 (14)	0·25000	0·64808 (28)	3·80 (16)
N1	0·33304 (8)	0·25000	0·01190 (16)	3·16 (7)
	0·33299 (10)	0·25000	0·01155 (19)	3·14 (11)
N2	0·44533 (9)	0·25000	0·50248 (16)	3·37 (7)
	0·44534 (10)	0·25000	0·50234 (19)	3·32 (11)
C1	0·49082 (4)	0·51087 (4)	0·23215 (9)	2·25 (3)
	0·49092 (6)	0·51090 (6)	0·23240 (12)	2·18 (7)
C2	0·61826 (4)	0·46424 (5)	0·24975 (10)	2·34 (3)
	0·61840 (7)	0·46418 (6)	0·24984 (13)	2·26 (7)
H1	0·783 (1)	0·496 (1)	0·198 (2)	5·5 (4)
	0·7845 (2)	0·4962 (1)	0·2006 (3)	4·3 (2)
H2	0·165 (1)	0·201 (1)	0·629 (2)	5·9 (4)
	0·1563 (2)	0·1875 (2)	0·6380 (4)	5·0 (2)
H3	0·293 (2)	0·250	0·897 (3)	5·2 (5)
	0·2864 (4)	0·2406 (15)	0·8892 (7)	6·1 (1)
H4	0·287 (2)	0·219 (2)	0·086 (4)	5·0 (7)
	0·2756 (4)	0·2134 (4)	0·1084 (8)	5·9 (5)
H5	0·379 (1)	0·304 (1)	0·003 (3)	8·4 (6)
	0·3965 (6)	0·3091 (7)	−0·0214 (1)	5·4 (7)
H55	–	–	–	–
	0·3666 (8)	0·3134 (7)	0·0627 (1)	7·7 (10)
H6	0·366 (2)	0·250	0·531 (3)	5·6 (5)
	0·3591 (4)	0·2411 (18)	0·5392 (6)	6·0 (11)
H7	0·487 (2)	0·250	0·600 (4)	6·7 (7)
	0·4898 (4)	0·2291 (9)	0·6235 (8)	6·6 (9)
H8	0·458 (1)	0·304 (1)	0·435 (2)	5·2 (3)
	0·4477 (10)	0·3221 (12)	0·4109 (22)	4·4 (8)
H88	–	–	–	–
	0·4827 (12)	0·3094 (14)	0·4394 (27)	6·4 (12)

that these conditions are not satisfied by one ammonium group, for which only one H atom lies on the mirror plane. This result is in agreement with Küpper's ideas.

Correction was performed for isotropic type-I extinction, Lorentzian mosaic-spread distribution (Becker & Coppens, 1974, 1975). Indicators of precision and accuracy are given in Table 1. The final positional atomic parameters and equivalent isotropic temperature factors are listed in Table 3.

Neutron refinements. The starting parameters were taken from the present X-ray data for non-H atoms, scattering lengths from Koester & Yelon (1982). The behaviour of one ammonium group observed in the X-ray data was confirmed by the neutron difference maps, *i.e.* H4 is certainly disordered. A summary of some neutron refinements is shown in Table 2. The model chosen is refinement 10 which consists of eight half H atoms in general positions for each ammonium

group. This choice is partially based on the values of indicators shown in Table 2. The choice is also based on the network of hydrogen bonds in which the ammonium groups are involved (see *Discussion*). When the Hamilton (1965) *R*-factor-ratio test is applied at the 0·001 significance level, the unconstrained model should not be rejected; however, as Baur & Tillmanns (1986) pointed out, the data are too large; consequently, this test will always be valid in negative cases, *i.e.* if it favours the constrained model, but the converse may not be true.

Later refinements were undertaken with γ tensors corresponding to both Edgeworth and Gram–Charlier expansions of the probability density functions. For all cases there were no significant improvements of the refinement indicators. The last cycles of the refinements were also undertaken with the data uncorrected for TDS. No significant change was found in the atomic positions; the maximum shift was $0·2\sigma$ ($0·006$ Å) for H88. However, the mean-square amplitudes along the three principal axes were systematically smaller than the corresponding values found using the TDS-corrected data: the maximum shift was $1·4\sigma$ ($0·0010$ Å^2) in U^2_{11} for both C atoms in the hydrogen oxalate group. These results are in agreement with Willis & Pryor (1975) who have pointed out that ignoring the TDS effect leads to an underestimate of the temperature factors.

The anisotropic extinction model used was type I (Becker & Coppens, 1974, 1975) and Lorentzian anisotropic angular mosaic distribution according to Thornley & Nelmes (1974). The final positional atomic parameters and equivalent isotropic temperature factors for refinement 10 are listed in Table 3.*

Discussion. A stereoscopic view of the contents of the unit cell is presented in Fig. 1. Interatomic distances

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* List of structure factors, anisotropic thermal parameters and powder diffraction data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51500 (77 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
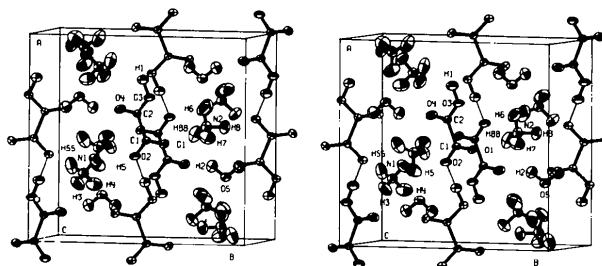

Fig. 1. The unit-cell contents of $NH_4HC_2O_4.1/2H_2O$. Here and in Fig. 2 the thermal vibration ellipsoids are drawn to include 50% probability (neutron data).

Table 4. *Interatomic distances* (Å) *and angles* (°)

The upper row refers to the X-ray data, the second row to the neutron data.

O1—C1	1·242 (1)	N1—H3	–
	1·238 (1)		1·000 (5)
O2—C1	1·259 (1)	N1—H4	–
	1·256 (1)		1·033 (5)
O3—C2	1·304 (1)	N1—H5	–
	1·299 (1)		1·046 (7)
O3—H1	–	N1—H55	–
	1·037 (2)		0·938 (9)
O4—C2	1·210 (1)	N2—H6	–
	1·205 (1)		1·008 (5)
C1—C2	1·548 (1)	N2—H7	–
	1·549 (1)		1·007 (6)
O5—H2	–	N2—H8	–
	0·970 (2)		1·091 (15)
		N2—H88	–
			0·949 (17)

O1—C1—O2	127·33 (5)	O3—C2—O4	125·35 (5)
	127·14 (8)		125·28 (9)
O1—C1—C2	118·12 (5)	O3—C2—C1	113·35 (5)
	118·21 (7)		113·43 (7)
O2—C1—C2	114·56 (5)	O4—C2—C1	121·30 (5)
	114·65 (7)		121·29 (8)
H2—O5—H2	–		
	105·4 (3)		
H3—N1—H4	–	H6—N2—H7	–
	105·7 (6)		107·2 (5)
H3—N1—H5	–	H6—N2—H8	–
	104·8 (9)		105·0 (12)
H3—H1—H55	–	H6—N2—H88	–
	115·6 (12)		117·1 (15)
H4—N1—H5	–	H7—N2—H8	–
	105·2 (5)		105·0 (9)
H4—N1H55	–	H7—H2—H88	–
	111·9 (7)		111·0 (11)
H5—N1—H55	–	H8—N2—H88	–
	112·9 (7)		110·7 (13)

Hydrogen sites in ammonium groups

H3···H3'	–	H6···H6'	–
	0·23 (4)		0·22 (4)
H4···H4'	0·77 (5)	H7···H7'	–
	0·90 (1)		0·52 (2)
H5···H55	–	H8···H88	–
	0·67 (1)		0·47 (2)

Hydrogen bonding

A—H···B	H···B	A···B	A—H···B
O3—H1···O2	–	2·563 (1)	–
	1·526 (2)	2·562 (1)	176·2 (2)
O5—H2···O1	–	2·782 (1)	–
	1·852 (2)	2·782 (2)	159·6 (2)
N1—H3···O5	–	2·871 (1)	–
	1·885 (5)	2·874 (2)	169·1 (15)
N1—H4···O4	–	2·949 (1)	–
	1·983 (5)	2·950 (2)	154·8 (4)
N1—H4···O4'	–	–	–
	2·595 (5)	–	99·7 (2)
N1—H5···O1	–	3·035 (1)	–
	2·024 (8)	3·037 (1)	162·3 (6)
N1—H5···O2	–	3·252 (1)*	–
	2·784 (7)*	3·256 (1)*	107·6 (5)
N1—H5···O3	–	3·065 (1)*	–
	2·541 (8)*	3·069 (1)*	110·6 (5)
N1—H55···O1	–	–	–
	2·551 (10)*	–	112·6 (7)
N1—H55···O2	–	–	–
	2·366 (9)	–	158·3 (8)
N1—H55···O3	–	–	–
	2·701 (9)*	–	104·2 (7)
N2—H6···O5	–	2·846 (1)	–
	1·858 (5)	2·848 (2)	166·7 (14)
N2—H7···O1	–	3·066 (1)	–
	2·181 (8)	3·067 (1)	145·8 (7)
N2—H7···O1'	–	–	–
	2·576 (9)	–	109·8 (7)
N2—H8···O2	–	2·877 (1)	–
	1·818 (15)	2·879 (1)	163·1 (10)
N2—H8···O4'	–	2·935 (1)	–
	2·309 (13)	2·937 (2)	114·7 (8)
N2—H88···O2'	–	–	–
	2·160 (17)	–	131·6 (11)
N2—H888···O4	–	–	–
	2·085 (15)	–	148·5 (13)

* The two longest O···H5 and O···H55 distances are not necessarily hydrogen bonds.

and bond angles are listed in Table 4. The hydrogen oxalate groups are linked together by hydrogen bonds and form infinite chains. The hydrogen oxalate group is planar; the maximum distance from the least-squares plane through the atoms is 0·006 (1) Å for O3. The angle between the planes of two consecutive hydrogen oxalate groups in a chain is 48·34°. One of the N—H bonds in each ammonium group is abnormally short (see Table 4). This feature always occurs for N1 for any refinement in Table 2. For N2 this phenomenon appears when a disordered model is suggested. However, if the N—H distances are corrected for riding motion, where the lighter H atom is assumed to be riding on the heavier N atom, then the N—H distances in both groups range from 0·991 for N2—H88 to 1·103 for N2—H8. The N1 group is coordinated by nine O atoms while N2 is coordinated by seven O atoms.

From diffraction studies alone, it is in general not possible to distinguish a static disorder from a dynamic one. A static disorder in which half of the ammonium groups has one orientation, as in Fig. 2(a), and the other half has the orientation given in Fig. 2(b), where both are distributed randomly through the crystal, might be a good model. However, inspection of Fig. 2 shows that the H atoms are relatively free to move from one orientation to the other. During these motions the total hydrogen-bond energy is approximately constant due to other similar possibilities of hydrogen bonding. For the H atoms which interact with more than one O atom, the weakest interaction in a given orientation of each ammonium group becomes the strongest interaction for the other orientation. When the ammonium groups move, H3, H4, H6 and H7 cross the mirror plane and the pairs H5–H55 and H8–H88 interchange positions

on the same side of the mirror plane. The rotation axes are N1—O5 and N2—O5 respectively. Refinements 9 and 10 differ from each other in the rotation axes, as in refinement 9 the axes are N1—H3 and N2—H6. To assume N—O5 as the rotation axis rather than N—H makes physical sense, since the motion of the ammonium groups will include some displacement of H3 and H6, therefore refinement 10 seems to be realistic.

The previous paragraph suggests the existence of different hydrogen-bonded systems which involve the ammonium groups. The cases of H3 and H6 are the simplest: the next O⋯H contacts, not shown in Table 4, have the values 2·66 (2) and 2·95 (2) Å, respectively, for H3 and H6, if they are located at one of the two equilibrium orientations (Fig. 2). These distances become longer, 2·774 (2) and 3·048 (4) Å, respectively, for H3 and H6, when the ammonium groups are rotated from their equilibrium orientations so that H3 and H6 lie on the mirror plane. Therefore, H3 and H6 form hydrogen bonds with one O atom. The atoms H4, H7 and the pair H8—H88 are involved in bifurcated hydrogen bonds. At first sight this condition is not satisfied by H4 and H7, because, for these two atoms, one O⋯H bond is too long and the corresponding

N—H⋯O angle is too bent, as is shown in Table 4 [a criterion for defining hydrogen bonds asserts that if an O⋯H contact is not longer than 2·4 Å, a hydrogen bond may occur, see Olovsson & Jönsson (1976, p. 402)]. However, if H4 or H7 lies on the mirror plane, each of them will be equidistant from two crystallographically equivalent O atoms and this distance becomes, approximately, equal to the mean value of the two O⋯H distances indicated in Table 4. Under these conditions, O4⋯H4 is 2·266 (5), O1⋯H7 is 2·380 (5) Å and the two corresponding N—H⋯O angles are, respectively, 129·7 (3) and 127·7 (2)°. Assuming that the electrostatic energy is the most important contribution to the total hydrogen-bond energy, if the second interaction were neglected in the disordered model its energy would be ~ 43% higher than the energy of the ordered model. However, if the two interactions are taken into account, the disordered model will have an energy ~ 0·8% lower than the ordered model. Therefore, these considerations lead us to conclude that H4 and H7 as well as H8 and H88 are involved in bifurcated hydrogen bonds. The case of the pair H5—H55 is more complicated. With the coordinates of H5 from the ordered model its distances to O1, O2 and O3 are, respectively, 2·231 (6), 2·583 (6) and 2·584 (6) Å. The corresponding N—H⋯O angles are 141·3 (5), 127·6 (5) and 111·6 (4)°, respectively. Such a situation prevents the determination with certainty of whether a second or even a third interaction exists, i.e. two of these three O⋯H distances are always too long. Possibly the principal reason for our difficulty in determining the type of hydrogen bond for H5 is the high coordination number of the N1 ammonium group.
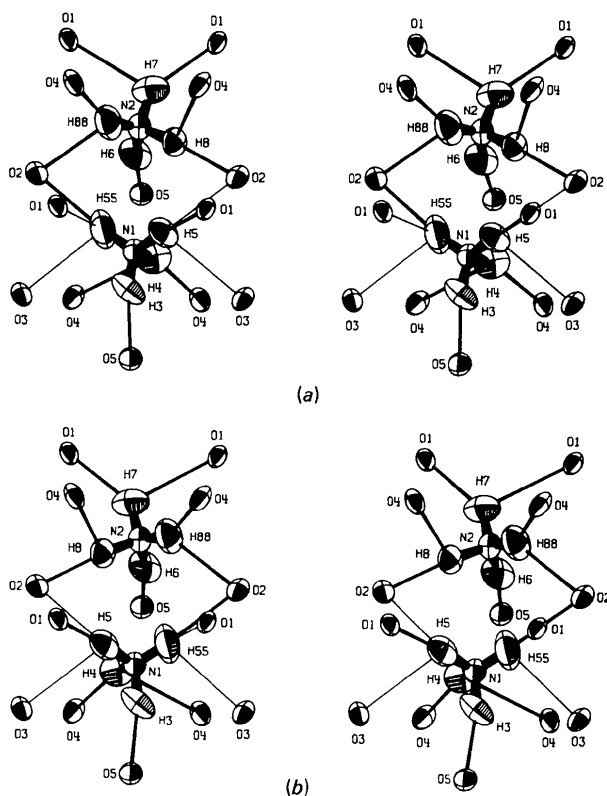
Fig. 2. Stereoscopic views of the two equilibrium orientations of the two independent ammonium groups and the network of N—H⋯O hydrogen bonds. O2⋯H5, O3⋯H5, O1⋯H55 and O3⋯H55 contacts are not necessarily hydrogen bonds (see Discussion).

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Structure of 1,4-Bis(2-pyridyl)-1,3-butadiyne

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Abstract. $C_{14}H_8N_2$, $M_r = 204$, m.p. 393 K, monoclinic, $P2_1/n$, $a = 6\cdot2411$ (7), $b = 3\cdot973$ (1), $c = 21\cdot467$ (3) Å, $\beta = 92\cdot77$ (1)°, $V = 531\cdot64$ Å^3, $Z = 2$, $D_x = 1\cdot274$, D_m(by flotation in aqueous KI) = $1\cdot282$ g cm^{-3}, λ(Mo $K\alpha$) = $0\cdot7107$ Å, $\mu = 0\cdot835$ cm^{-1}, $F(000) = 212$, $T = 295$ K, $R = 0\cdot0411$ for 687 observed reflections. The crystals undergo thermal polymerization to form a coloured amorphous polymer, most likely a poly-diacetylene, although the reacting atoms are separated by $4\cdot237$ (3) Å. The bond lengths C(6)–C(7) = $1\cdot192$ (3) and C(5)–C(6) = $1\cdot442$ (3) Å. The pyridyl rings are planar and parallel to each other.

Introduction. Diacetylenes (R–C≡C–C≡C–R, where R is a substituent group) undergo polymerization in the solid state upon thermal stimulation or exposure to high-energy radiation. Not all diacetylenes are reactive, only those diacetylenes polymerize which have suitable packing features in the crystals (Baughman, 1974; Wegner, 1977; Bloor, 1982). The substituent group R influences the packing and reactivity in a subtle manner through steric and electronic effects. Our study is directed towards examining the reactivity of diacetylenes in which the substituent R is an aromatic heterocycle in formal conjugation with the diacetylene unit. In this paper we report the crystal structure of the title compound (DP), which is found to be reactive

despite the reacting atoms being separated by more than $4\cdot0$ Å.

Experimental. The title compound was prepared by coupling 2-ethynylpyridine using the method of Fritzche & Hunig (1972). Crystallization from acetone gave colourless needle-shaped crystals. Preliminary X-ray studies indicated that the crystal undergoes some changes on exposure to X-rays. However, crystals which have been annealed for some time remain unchanged on exposure to X-rays. The crystals, on annealing, acquire a light-brown colour due to the formation of a small amount of polymer. Crystals used for X-ray study were annealed for 10 h at 388 K and are estimated to have less than 5% polymer. The presence of a small amount of the polymer did not interfere in the structure determination of the monomer (see below). A crystal of dimensions $0\cdot20 \times 0\cdot25 \times 0\cdot32$ mm was selected for data collection with an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scan. Unit-cell parameters, obtained by oscillation and Weissenberg photographs, were refined by least-squares analysis using 21 reflections, $5 < \theta < 12°$, on the diffractometer. Intensities of two standard reflections recorded every 30 min showed no significant changes. Data were collected in the range $2 < \theta < 25°$ (resolution $d = 0\cdot84$ Å, $h_{max} = 7$, $k_{max} = 4$, $l_{min} = -25$, $l_{max} = 25$). 1162 reflections gave 1083 unique reflections after averaging