

Hydrogen-Bond Studies. LXXV.* An X-ray Diffraction Study of Normal and Deuterated Hydrazinium Hydrogen Oxalate, $\text{N}_2\text{H}_5\text{HC}_2\text{O}_4$ and $\text{N}_2\text{D}_5\text{DC}_2\text{O}_4$

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The crystal structures of normal and deuterated hydrazinium hydrogen oxalate, $\text{N}_2\text{H}_5\text{HC}_2\text{O}_4$, have been investigated using three-dimensional single-crystal X-ray data collected at 25°C using an automatic Stoe-Philips four-circle diffractometer. Identical procedures were followed to provide an ideal experimental basis for comparison. Both unit cells are monoclinic containing two formula units. The cell dimensions found for $\text{N}_2\text{H}_5\text{HC}_2\text{O}_4$ are: $a = 3.5792$ (3), $b = 13.3228$ (16), $c = 5.0965$ (3) Å, $\beta = 102.600$ (6)°, $V = 237.177$ Å³; and for $\text{N}_2\text{D}_5\text{DC}_2\text{O}_4$: $a = 3.5858$ (5), $b = 13.3085$ (16), $c = 5.1001$ (5) Å, $\beta = 102.488$ (9)°, $V = 237.627$ Å³. The most appropriate space group for $\text{N}_2\text{H}_5\text{HC}_2\text{O}_4$ was confirmed to be $P2_1/m$, whereas $\text{N}_2\text{D}_5\text{DC}_2\text{O}_4$ exhibited the lower symmetry space group $P2_1$. Deuteration, while preserving most of the general features of the structure, thus renders it non-centrosymmetric. The $\text{O}\cdots\text{H}\cdots\text{O}$ symmetric hydrogen bond linking the hydrogen oxalate ions to form chains in $\text{N}_2\text{H}_5\text{HC}_2\text{O}_4$ increases in length from 2.457 (2) to 2.466 (2) Å on deuteration. Furthermore, the virtually planar oxalate group in $\text{N}_2\text{H}_5\text{HC}_2\text{O}_4$ [dihedral twist: 0.1 (2)°] develops a twist of 1.4 (2)° in $\text{N}_2\text{D}_5\text{DC}_2\text{O}_4$. Evidence is also found to suggest that the deuterium atom in the $\text{O}\cdots\text{O}$ bond is slightly off-centre. The changes in the $\text{N}-\text{H}\cdots\text{O}$ bond lengths (up to 0.063 Å) are greater than those normally accompanying a deuteration and appear both as expansions and contractions. The final conventional R values obtained for the refinements of $\text{N}_2\text{H}_5\text{HC}_2\text{O}_4$ and $\text{N}_2\text{D}_5\text{DC}_2\text{O}_4$ were 0.034 and 0.033 respectively.

Introduction

Hydrazinium hydrogen oxalate has already been the subject of extensive studies at this Institute. An X-ray diffraction structure determination by Ahmed, Liminga & Olovsson (1968) followed by a neutron diffraction study by Nilsson, Liminga & Olovsson (1968) established the existence of N_2H_5^+ and HC_2O_4^- ions in the room-temperature crystal structure. A proton magnetic resonance investigation by Tegenfeldt & Olovsson (1971) has further shown that the NH_3 end of the N_2H_5^+ ion reorients rapidly about the $\text{N}-\text{N}$ bond. The feasibility of such movements has also been demonstrated in electrostatic calculations made by Lundgren, Liminga & Olovsson (1971). It was, however, a comparative infrared-spectroscopic study of the normal and deuterated compounds down to liquid-nitrogen temperature (Lindgren, de Villepin & Novak, 1969) which first awakened us to the need for an investigation of the deuterated crystal structure. Significant differences were observed in the low-temperature spectra, and these were found to persist, though to a lesser extent, even at room temperature. Continual cracking of single crystals of both $\text{N}_2\text{H}_5\text{HC}_2\text{O}_4$ and $\text{N}_2\text{D}_5\text{DC}_2\text{O}_4$ on cooling forced the postponement of a low-temperature study. Instead, a study of the room-temperature situation was undertaken.

In containing a ~ 2.45 Å symmetric $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bond, it was appreciated that this compound also presented a most interesting subject for an isotope-

effect study. This value falls precisely in that region of symmetric $\text{O}\cdots\text{H}\cdots\text{O}$ bond lengths where the form of the associated potential is in greatest doubt, *cf.* Rundle (1964).

In the following, hydrazinium hydrogen oxalate will be abbreviated to HYHOX and its deuterated counterpart to DYDOX.

Crystal data

Hydrazinium hydrogen oxalate, $\text{N}_2\text{H}_5\text{HC}_2\text{O}_4$. F.W. 122.09. Monoclinic, $P2_1/m$, $a = 3.5792$ (3),* $b = 13.3228$ (16), $c = 5.0965$ (3) Å, $\beta = 102.600$ (6)°, $V = 237.177$ Å³ at 25°C. $Z = 2$, $D_x = 1.709$ g cm⁻³, μ_{calc} (Mo $K\alpha$) = 1.774 cm⁻¹.

Deuterated hydrazinium hydrogen oxalate, $\text{N}_2\text{D}_5\text{DC}_2\text{O}_4$. F.W. 128.14. Monoclinic, $P2_1$, $a = 3.5858$ (5), $b = 13.3085$ (16), $c = 5.1001$ (5) Å, $\beta = 102.488$ (9)°, $V = 237.627$ Å³ at 25°C. $Z = 2$, $D_x = 1.791$ g cm⁻³, μ_{calc} (Mo $K\alpha$) = 1.804 cm⁻¹.

Experimental

Clear rod-shaped crystals of HYHOX were obtained as described by Ahmed *et al.* (1968). The DYDOX crystals were obtained by repeated recrystallizations from heavy water (>99.9%). The crystals so formed had roughly the same morphology as the HYHOX crystals. Their ultimate degree of deuteration was es-

* Part LXXIV: *Mol. Phys.* (1973). In the press.

* Numbers in parentheses represent estimated standard deviations on the least significant digits.

timated to be better than 95%. This value was arrived at by comparing the peak heights for certain of the N–H and N–D stretching modes in the infrared spectrum of DYDOX. In practice, it was the N–H modes in the N–H...O bonds from the NH₂ end of the N₂H₅⁺ ion which were involved in the measurement. The assumption was then made that a random distribution of H atoms pervades all D-atom sites throughout the crystal.

Suitable single crystals of both compounds were selected for data collection. The HYHOX crystal was wedge-shaped: 0.15 mm long and having a cross section of 0.015 mm². The DYDOX crystal was lath-like in form, measuring 0.53 × 0.17 × 0.10 mm. To preserve the high degree of deuteration, the crystal was hastily sealed in a thin-walled silica glass capillary of approximate diameter 0.2 mm.

The cell parameters were measured using a Guinier–Hägg powder camera calibrated with silicon [$a = 5.43054$ Å, $\lambda(\text{Cu } K\alpha_1) = 1.54051$ Å]. The films provided 50 and 48 observed θ values for HYHOX and DYDOX respectively. These were then used in a least-squares refinement program.

A number of reconnaissance Weissenberg and Laue photographs were taken to check the crystal quality. Data collections were carried out at 25°C using a four-circle Stoe–Philips X-ray diffractometer as described by Thomas (1972). Graphite monochromatized Mo $K\alpha$ radiation was used. All reflexions within the molybdenum half-sphere were collected out to $\sin \theta/\lambda = 0.7035$ Å⁻¹ for both crystals.

The integrated peak intensities were corrected for background and assigned standard deviations $\sigma_c(I)$ based on Poisson counting statistics using the expressions provided by Jönsson & Liminga (1971). Only small random fluctuations [$\sim \pm 2\sigma_c(I)$] were observed in the intensities of the three standard reflexions measured every 40 reflexions during the HYHOX data collection and every 20 reflexions during the DYDOX data collection. Corrections for Lorentz, polarization and absorption effects were made, resulting in two sets of F_o^2 and $\sigma_c(F_o^2)$. An explicit description of both crystals was possible in terms of their rational boundary planes. Resulting transmission factors for HYHOX were in the range 0.977–0.981, and for DYDOX in the range 0.969–0.983. The calculated effective path length

Table 1. *The agreement factors at successive stages in the refinements*

The expressions for $R(F^2)$ and $R_w(F^2)$ are given in the text.

Refinement Number	Parameters refined	HYHOX				DYDOX			
		$P2_1/m$ $R(F^2)$	$R_w(F^2)$	$P2_1$ $R(F^2)$	$R_w(F^2)$	$P2_1/m$ $R(F^2)$	$R_w(F^2)$	$P2_1$ $R(F^2)$	$R_w(F^2)$
1	Scale factor, positional and isotropic thermal parameters for heavy atoms only (3 cycles)	0.235	0.429	0.283	0.409	–	–	0.214	0.411
2	As (1) but anisotropic thermal parameters for heavy atoms (3 cycles)	0.105	0.166	0.151	0.160	0.138	0.340	0.099	0.154
3	As (2) + positional and isotropic thermal parameters for H atoms [H(4) omitted] (3 cycles)	0.059	0.108	0.056	0.091	–	–	0.062	0.103
4	As (3) + isotropic extinction parameters (2 cycles)	0.075	0.110	0.073	0.092	–	–	–	–
5	As (3) + H(4) fixed at origin and its isotropic thermal parameters refined (2 cycles)	0.055	0.104	–	–	0.117	0.320	–	–
6	As (3) + positional and isotropic thermal parameters refined for H(4) (3 cycles)	–	–	–	–	–	–	0.059	0.096
7	As (6) + isotropic extinction parameter (2 cycles)	–	–	–	–	–	–	0.056	0.096
8	As (6) but using a disordered model for H(4) and D(4). Only positional parameters refined (2 cycles)	–	–	0.050	0.081	–	–	0.058	0.096*
9	As (8) but an isotropic thermal parameter also refined for H(4)/2 and D(4)/2 (2 cycles)	0.054	0.101*	0.049	0.080	–	–	0.058	0.096†

* Final structural model chosen.

† Very large standard deviations on $B[\text{D}(4)/2]$ values.

within the crystal was saved for each reflexion, to be used later in investigating for possible extinction effects in the data.

The F_o^2 values for reflexions of type hkl and $h\bar{k}l$ were averaged together along with their path lengths, and an appropriately reduced $\sigma_c(F_o^2)$ calculated. After confirming the $k=2n+1$ absence condition on $0k0$ reflexions, these were removed from the data sets. None had I values in excess of $3\sigma(I)$. Altogether 707 independent reflexions were measured for HYHOX, of which 632 had F_o^2 values in excess of $2\sigma_c(F_o^2)$ and were used in the least-squares refinements. The corresponding numbers for DYDOX were 719 and 689 respectively.

Refinements

HYHOX

The similarity between the $P2_1$ and $P2_1/m$ refinements of HYHOX as performed by Nilsson *et al.* (1968) motivated a systematic reinvestigation of the problem. A series of refinements was performed for both space groups. In $P2_1/m$ the heavy-atom positional parameters of Ahmed *et al.* (1968) were taken as starting values. The same (x, y, z) values together with a set shifted slightly (and randomly) from the cor-

responding $(-x, -y, -z)$ positions for the O and C atoms were used as starting values in the $P2_1$ series. Full-matrix least-squares refinements were performed minimizing the function $\sum w(|F_o^2| - |F_c^2|)^2$. In the final refinements the weighting scheme was modified such that $w = 1/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = \sigma_c(F_o^2) + (0.05F_o^2)^2$. This is intended to take account of the proportionately larger effects of random errors on the intensities of stronger reflexions. The suitability of such a weighting scheme was checked after the final refinements. The progress of the refinements are summarized in Table 1 in which the R values given were calculated from the expressions:

$$R(F^2) = \frac{\sum (|F_o^2| - |F_c^2|)}{\sum |F_o^2|}$$

and

$$R_w(F^2) = \left[\frac{\sum w(|F_o^2| - |F_c^2|)^2}{\sum w|F_o^4|} \right]^{1/2}.$$

In both cases the hydrogen atoms were located in difference-Fourier syntheses following anisotropic-temperature-factor refinement of the heavy atoms. A Hamilton significance test (Hamilton, 1965), applied to the R value ratio of the final $P2_1$ and $P2_1/m$ refinements, indicated a marginal physical significance for the non-centrosymmetric space group, $P2_1$. However,

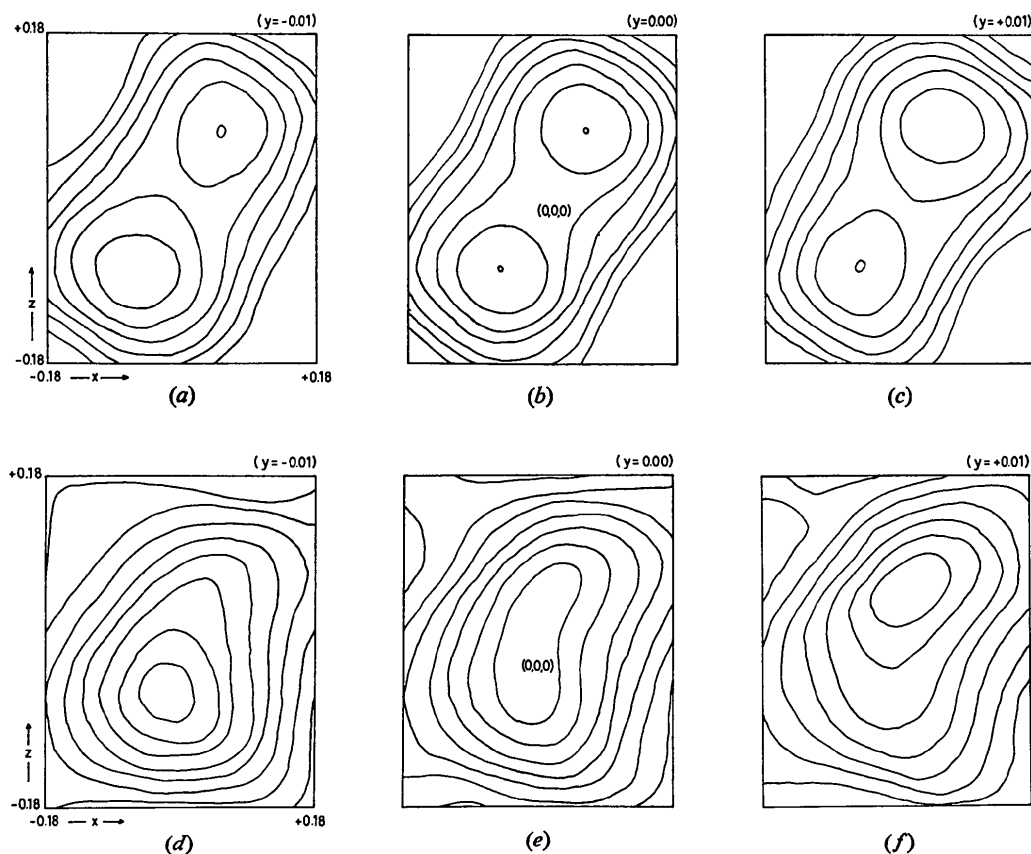


Fig. 1. Difference syntheses in the region of the origin after refinements 3 (see Table 1). In all maps the contours are drawn starting at $0.10 \text{ e } \text{\AA}^{-3}$ and at intervals of $0.05 \text{ e } \text{\AA}^{-3}$; (a)–(c) HYHOX ($P2_1/m$); interpolated peak centres at $\pm(0.055, 0.003, 0.080)$; (d)–(f) DYDOX ($P2_1$); interpolated peak centres at $(0.018, 0.006, 0.056)$ and $(-0.017, -0.013, -0.060)$.

in view of the large standard deviations (three to six times larger than for $P2_1/m$) and the extremely high correlations between the corresponding parameters of nearly centrosymmetrically related pairs of atoms (up to 96%), the significance-test prediction was overruled and preference given to the centrosymmetric alternative. The difficulty – indeed, perhaps the impossibility – of distinguishing absolutely between centro- and non-centrosymmetry in the presence of inverse overlap has been discussed theoretically by Srinivasan (1961), and well exemplified in the case of potassium hydrogen malonate by Parthasarathy, Sime & Speakman (1969).

A disordered arrangement for H(4) was chosen in the final refinement in $P2_1/m$, as suggested by the two completely resolved (symmetry-related) peaks of height $0.40 \text{ e } \text{Å}^{-3}$ found near the origin in the difference synthesis following refinement 3 (see Fig. 1). These peaks show a striking resemblance to those found recently in a 2.48 Å symmetric O–H–O bond in potassium hydrogen meso-tartrate (Kroon & Kanters, 1972). That the peak associated with H(4) should comprise two (equal) maxima merely satisfies symmetry requirements and is not in itself conclusive proof of *real* disorder. It should be noted, however, that the peaks were well resolved (separation: 0.83 Å) and lay in positions generally consistent with a disorder situation; remembering, of course, the usual X–H shortening effect inherent in X-ray analysis. Similarly placed

Table 2. Atomic coordinates: for heavy atoms ($\times 10^5$), for hydrogen and deuterium ($\times 10^3$)

HYHOX			
	<i>x</i>	<i>y</i>	<i>z</i>
C	61894 (28)	2499 (7)	62876 (17)
N(1)	29543 (45)	25000	8132 (30)
N(2)	10308 (44)	25000	30121 (30)
O(1)	58959 (26)	11514 (6)	66648 (16)
O(2)	83703 (25)	–3644 (6)	78385 (15)
H(1)	222 (6)	198 (2)	–4 (4)
H(2)	188 (5)	195 (2)	394 (4)
H(3)	–126 (9)	250	251 (5)
H(4)/2	70 (13)	3 (5)	100 (8)
DYDOX			
	<i>x</i>	<i>y</i>	<i>z</i>
C	65074 (55)	2479 (28)	63543 (40)
C'	–58907 (51)	–2488 (30)	–62180 (40)
N(1)	29790 (54)	25000	7997 (31)
N(2)	10461 (50)	24687 (29)	29836 (34)
O(1)	62649 (53)	11485 (30)	67220 (36)
O(1)'	–55604 (53)	–11552 (31)	–66016 (35)
O(2)	86544 (49)	–3749 (25)	79145 (34)
O(2)'	–80688 (45)	3562 (25)	–77564 (33)
D(1)	276 (11)	194 (4)	–3 (10)
D(1)'	204 (10)	298 (4)	–8 (8)
D(2)	160 (8)	190 (3)	354 (6)
D(2)'	189 (9)	297 (3)	414 (7)
D(3)	–123 (12)	243 (5)	251 (7)
D(4)/2	27 (33)	–18 (8)	–103 (33)
D(4)'/2	97 (27)	–7 (9)	52 (30)

Table 3. Anisotropic thermal parameters ($\times 10^4$)

The form of the temperature factor is: $\exp [-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$. The r.m.s. components ($R_i \times 10^3 \text{ Å}$) of thermal displacement along the principal axes of the thermal vibration ellipsoids are also given along with the isotropic thermal parameters ($B \text{ Å}^2$) for the hydrogen and deuterium atoms.

HYHOX										
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	<i>B</i>	<i>R</i> ₁	<i>R</i> ₂	<i>R</i> ₃
C	408 (8)	22 (1)	108 (3)	2 (1)	–17 (4)	–3 (1)		110 (2)	141 (2)	171 (2)
N(1)	635 (13)	26 (1)	215 (5)	0	114 (6)	0		152 (2)	160 (2)	199 (2)
N(2)	438 (12)	23 (1)	266 (6)	0	112 (6)	0		145 (2)	157 (2)	185 (2)
O(1)	793 (9)	22 (1)	200 (3)	20 (1)	–92 (4)	–16 (1)		128 (2)	149 (1)	251 (1)
O(2)	643 (8)	23 (1)	160 (3)	13 (1)	–123 (4)	–5 (1)		114 (2)	144 (1)	235 (1)
H(1)							4.1 (4)			
H(2)							3.2 (3)			
H(3)							2.8 (5)			
H(4)/2							5.1 (10)			
DYDOX										
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	<i>B</i>	<i>R</i> ₁	<i>R</i> ₂	<i>R</i> ₃
C	451 (12)	25 (1)	137 (6)	–5 (3)	–1 (6)	–10 (2)		121 (3)	155 (3)	177 (2)
C'	455 (13)	22 (1)	145 (6)	4 (3)	4 (6)	–2 (2)		131 (3)	139 (3)	178 (2)
N(1)	714 (15)	26 (1)	244 (5)	–6 (4)	133 (7)	–8 (3)		149 (3)	172 (3)	212 (2)
N(2)	502 (13)	23 (1)	308 (6)	0 (3)	134 (7)	7 (3)		142 (3)	168 (2)	200 (2)
O(1)	861 (15)	22 (1)	240 (6)	17 (3)	–61 (7)	–16 (2)		132 (3)	164 (2)	256 (2)
O(1)'	847 (15)	25 (1)	240 (7)	28 (3)	–70 (7)	–18 (2)		137 (3)	163 (2)	258 (2)
O(2)	687 (12)	24 (1)	207 (6)	13 (2)	–89 (7)	–1 (2)		139 (2)	149 (3)	237 (2)
O(2)'	687 (13)	25 (1)	192 (6)	10 (3)	–117 (7)	–8 (2)		128 (3)	149 (3)	242 (2)
D(1)							4.2 (8)			
D(1)'							2.9 (7)			
D(2)							1.9 (5)			
D(2)'							2.6 (6)			
D(3)							3.5 (6)			
D(4)/2							5.0*			
D(4)'/2							5.0*			

* Not refined

Table 4. Observed and calculated structure factors for N₂H₅HC₂O₄ and N₂D₅DC₂O₄

The four columns are, in order, the indices k and l, F_o (×100) and F_c (×100). The reflexions 10 $\bar{1}$ and all reflexions with F² < 2σ_c(F²) are marked with an asterisk and were not included in the least-squares refinements.

N₂H₅HC₂O₄

Table of observed and calculated structure factors for N2H5HC2O4. Columns include indices k and l, Fo (x100), and Fc (x100). The table contains multiple columns of data for different reflections, with some values marked with an asterisk to indicate they were excluded from refinements.

N₂D₅DC₂O₄

Table of observed and calculated structure factors for N2D5DC2O4. Columns include indices k and l, Fo (x100), and Fc (x100). The table contains multiple columns of data for different reflections, with some values marked with an asterisk to indicate they were excluded from refinements.

double peaks (of heights 0.34 and 0.36 e Å⁻³) were also found to represent H(4) in the difference synthesis following refinement in $P2_1$. However, these could again be artifacts of the high correlation in the refinement; the structure refined being so near centrosymmetric. The final shifts in the disordered $P2_1/m$ refinement were all $\lesssim 0.01\sigma$ for the heavy-atom parameters and $\lesssim 0.1\sigma$ for the hydrogen-atom parameters. The maximum charge density remaining in the difference synthesis in the region of the O(2)–H(4)/2–H(4)/2–O(2) bond was 0.09 e Å⁻³. The final conventional $R(F)$ and $R_w(F)$ values were 0.034 and 0.056 respectively.

The presence of extinction effects in the data was investigated by including an isotropic extinction parameter g (Coppens & Hamilton, 1970) in a further refinement. This resulted in a significant deterioration in R value as a result of over-correction of most of the strong reflexions in the data. Only the very strong 10 $\bar{1}$ reflexion appeared to be genuinely subject to extinction effects. The only allowance made for extinction was therefore the omission of the 10 $\bar{1}$ reflexion. It had, in fact, already been omitted from all previous refinements on suspicion of being seriously extinction affected.

The resulting positional and thermal parameters are given in Tables 2 and 3. The corresponding observed and calculated structure factors are provided in Table 4.

It is relevant here to note that in neither of the earlier studies of HYHOX was a disorder site observed for H(4). This is perhaps not so surprising in the case of the X-ray study (Ahmed *et al.*, 1968) which employed film data. On the other hand, some indication might have been expected from the neutron diffraction study (Nilsson *et al.*, 1968). That none was found can depend

on the essential difference between the X-ray and neutron technique. Neutrons may not succeed in resolving two disordered proton sites separated by ~ 0.25 Å (*cf.* McGaw & Ibers, 1963), whereas an accurate X-ray study should resolve the more separated (0.6–0.7 Å) double peaks of the electron distribution associated with such an arrangement. Otherwise, it is notable that the atomic positions obtained here for the heavy atoms all agree with the results of both previous studies to within 2σ , where σ is the combined standard deviation for the two investigations being compared.

DYDOX

Expecting a preference for the centrosymmetric space group to apply also for DYDOX, the refinement was begun using the same starting parameters as for

Table 5. *Interatomic distances (Å) and angles (°)*

(i) Within the N₂H₅⁺ and HC₂O₄⁻ ions.

HYHOX		DYDOX	
N(1)–N(2)	1.438 (2)	N(1)–N(2)	1.434 (2)
C—C	1.550 (2)	C—C'	1.552 (2)
C—O(1)	1.224 (1)	C—O(1)	1.219 (3)
		C'—O(1')	1.232 (3)
C—O(2)	1.279 (1)	C—O(2)	1.284 (3)
		C'—O(2')	1.268 (3)
O(1)–C–O(2)	126.33 (9)	O(1)–C–O(2)	126.34 (19)
C—C–O(1)	120.27 (10)	O(1)–C'–O(2')	126.22 (18)
		C'—C–O(1)	120.25 (16)
		C—C'–O(1')	119.77 (15)
C—C–O(2)	113.39 (10)	C'—C–O(2)	113.41 (15)
		C—C'–O(2')	114.02 (16)

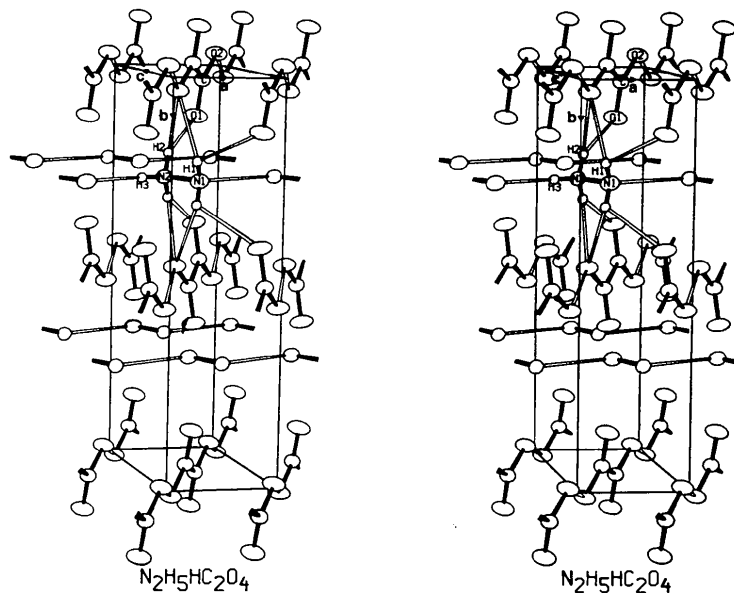


Fig. 2. A stereoscopic illustration of the structure of HYHOX. Labelling is carried by the atoms of the asymmetric unit; atom H(4) is omitted. Covalent bonds are solid and hydrogen bonds open. Thermal ellipsoids are drawn here and elsewhere for the non-hydrogen atoms to include 50% probability.

Table 5 (*cont.*)

(ii) Within the hydrogen bonds.

HYHOX		DYDOX	
N(1)···O(1)	3.127 (2)	N(1)···O(1)	3.164 (2)
N(1)—H(1)	0.83 (2)	N(1)—D(1)	0.85 (5)
H(1)···O(1)	2.59 (2)	D(1)···O(1)	2.52 (5)
N(1)—H(1)···O(1)	123.1 (1.7)	N(1)—D(1)···O(1)	133.7 (4.0)
N(1)···O(2)	2.989 (1)	N(1)···O(2)	2.990 (2)
N(1)—H(1)	0.83 (2)	N(1)—D(1)'	0.81 (5)
H(1)···O(2)	2.45 (2)	D(1)···O(2)	2.49 (4)
N(1)—H(1)···O(2)	122.9 (1.6)	N(1)—D(1)'···O(2)	121.1 (3.2)
N(2)···O(1)	2.883 (2)	N(2)···O(1)	2.946 (3)
N(2)—H(2)	0.89 (2)	N(2)—D(2)	0.81 (4)
H(2)···O(1)	2.06 (2)	D(2)···O(1)	2.29 (3)
N(2)—H(2)···O(1)	153.0 (1.7)	N(2)—D(2)···O(1)	137.6 (2.9)
N(2)···O(2)	2.893 (1)	N(2)···O(2)	2.912 (3)
N(2)—H(2)	0.89 (2)	N(2)—D(2)'	0.90 (4)
H(2)···O(2)	2.29 (2)	D(2)'···O(2)	2.43 (4)
N(2)—H(2)···O(2)	124.6 (1.5)	N(2)—D(2)'···O(2)	114.0 (2.6)
N(1)···N(2)	2.863 (2)	N(1)···N(2)	2.866 (3)
N(2)—H(3)	0.80 (3)	N(2)—D(3)	0.80 (4)
H(3)···N(1)	2.06 (3)	D(3)···N(1)	2.07 (4)
N(2)—H(3)···N(1)	173.7 (2.5)	N(2)—D(3)···N(1)	170.5 (4.9)
O(2)···O(2)	2.457 (1)	O(2)···O(2)'	2.466 (2)
O(2)—H(4)/2	0.76 (5)	O(2)—D(4)/2	0.75 (16)
H(4)/2···O(2)	1.72 (4)	D(4)/2···O(2)'	1.79 (16)
H(4)/2···H(4)/2	1.04 (7)	D(4)/2···D(4)/2	0.79 (11)
O(2)—H(4)/2···O(2)	161.0 (6.5)	O(2)—D(4)/2···O(2)'	149.1 (9.0)
		O(2)'—D(4)'/2	1.04 (15)
		D(4)'/2···O(2)	1.46 (15)
		O(2)'—D(4)'/2···O(2)	159.4 (10.7)

HYHOX and assuming the space group $P2_1/m$. It was soon clear, however, that this assumption was in error. Although refinement was possible and reasonable D-atom positions resulted, no satisfactory convergence could be obtained and the final $R(F^2)$ and $R_w(F^2)$ values stabilized at 0.117 and 0.320 respectively. At this point ~ 60 reflexions had $|F_o^2 - F_c^2|$ values in excess of $10\sigma(F_o^2)$.

The situation improved dramatically, however, on refining in the non-centrosymmetric space group $P2_1$, using the same starting values as for the HYHOX $P2_1$ refinement. The progress of these refinements is shown in Table 1. Here again, the D-atom starting positions [except for D(4)] were located in a difference Fourier synthesis. A disordered arrangement for D(4) was again suggested by the presence of two peaks (see Fig. 1) of heights 0.47 and 0.43 $e \text{ \AA}^{-3}$ in the difference synthesis [representing D(4)/2 and D(4)'/2, respectively]. The peaks were here less well resolved than for HYHOX, their centres lying 0.63 \AA apart. It was also noted that the midpoint between the two peaks had shifted towards O(2). A statistically centrosymmetric arrangement is clearly no longer a direct requirement of symmetry. On the other hand, the appearance of two peaks need not imply a *real* disorder situation. It could still be an artifact of the approximately centrosymmetric environment of D(4) and the attendant high correlation effects, *cf.* the $P2_1$ refinement of HYHOX. The O(2)—D(4)/2—D(4)'/2—O(2)' arrangement was only marginally preferable to O(2)—D(4)—O(2)' on the basis of a Hamilton significance test on the R_w index for refinement 8 with respect to refinement 6. It is chosen

as the final *most representative model* of the structure on the basis of the difference map evidence. The existence or otherwise of a *real* disorder associated with D(4) cannot be ascertained here, however.

The same weighting scheme was used in the final refinements as for the HYHOX data. The correlation coefficients in the final refinement for DYDOX in $P2_1$ (up to 89%) were considerably higher than in the $P2_1/m$ refinement of HYHOX (all under 50%). This is predictable in view of the approximate centre of symmetry in the asymmetric unit of the structure. The standard deviations in the refined parameters are consequently up to five times greater than those obtained for HYHOX. The final shifts were all $\lesssim 0.2\sigma$ for the heavy-atom parameters and $\lesssim 0.5\sigma$ for the deuterium-atom parameters. The maximum charge density remaining in the difference synthesis in the region of the O(2)—D(4)/2—D(4)'/2—O(2)' bond was 0.22 $e \text{ \AA}^{-3}$. The final more conventional $R(F)$ and $R_w(F)$ values were 0.033 and 0.049 respectively.

An exactly comparable extinction situation as in HYHOX was discovered in the DYDOX data. It was therefore treated in an identical manner.

The final positional and thermal parameters are given in Tables 2 and 3, and the corresponding observed and calculated structure factors are provided in Table 4. The atomic scattering factors used for C, N and O were those suggested by Hanson, Herman, Lea & Skillman (1964). The H spherical scattering factors used were those proposed by Stewart, Davidson & Simpson (1965). The calculations were all performed using the programs described by Thomas (1972).

Discussion

General

Despite their nominally different space-group assignments, the two structures are intimately related. The HYHOX structure is depicted in Fig. 2; the bond distances and angles found for HYHOX and DYDOX are given in Table 5. Both structures comprise chains of hydrogen-bond linked HC_2O_4^- ions running in the $[101]$ direction, with the near planar ions (see later) lying in the $(10\bar{1})$ plane. These chains are linked *via* the N_2H_5^+ ions by means of $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds. The N_2H_5^+ ions are themselves linked *via* $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds to form zigzag chains running in the $[100]$ direction. In HYHOX ($P2_1/m$) the N atoms lie on the mirror planes at $y=\frac{1}{4}$ and $y=\frac{3}{4}$. In DYDOX ($P2_1$), with atom N(1) constrained to lie in the $y=\frac{1}{4}$ plane, the refined position of N(2) is only $0.0031(3)$ Å out of this plane. A more detailed discussion of the HYHOX structure has been given by Nilsson *et al.* (1968).

It can be seen from Table 5 that the most noticeable differences between the two refined structures occur in the $\text{N}-\text{H}\cdots\text{O}$ hydrogen-bond linkages between the HC_2O_4^- chains and the N_2H_5^+ chains. These changes (see Fig. 3) accompany the disappearance of the mirror symmetry constraint on deuteration, with the result that the $\text{N}-\text{H}\cdots\text{O}$ bonds above and below the $y=\frac{1}{4}$ and $y=\frac{3}{4}$ planes are no longer equivalent. The length changes fall in the range -0.045 to $+0.063$ Å. More significant, however, is the apparent introduction of some degree of asymmetric character into the previously symmetric $\text{O}\cdots\text{O}$ hydrogen bonds linking the oxalate groups. The direct evidence for this [the pair of

peaks representing D(4) in the difference synthesis (Fig. 1) lay nearer O(2) than O(2)' and the stronger peak (by 10%) was that nearer O(2)] is hardly convincing. The length increase in the $\text{O}\cdots\text{O}$ bond, from $2.457(2)$ Å in HYHOX to $2.466(2)$ Å in DYDOX, is also only marginally significant. Strong indirect evidence is found, however, in the changes which occur in the C–O distances within the oxalate group on deuteration (see Fig. 4). The C–O(2) distance in DYDOX of $1.284(3)$ Å approaches C–O distances we have found in HC_2O_4^- chains where the oxygen atom functions as hydrogen-bond donor in an asymmetric hydrogen bond linking the ions, *cf.* 1.313 Å in $\text{NaHC}_2\text{O}_4\cdot\text{H}_2\text{O}$ (Tellgren & Olovsson, 1971), 1.309 Å in $\text{LiHC}_2\text{O}_4\cdot\text{H}_2\text{O}$ (Thomas, 1972), 1.291 Å in $(\text{CH}_3)\text{NH}_3\text{HC}_2\text{O}_4$ and 1.295 Å in $(\text{CH}_3)_2\text{NH}_2\text{HC}_2\text{O}_4$ (Thomas, 1973). Similarly, the C'–O(2)' distance in DYDOX [$1.268(3)$ Å] tends towards C–O distances found in the same type of chain but where the oxygen atom is now the hydrogen-bond acceptor, *cf.* 1.251 Å in $\text{NaHC}_2\text{O}_4\cdot\text{H}_2\text{O}$, 1.259 Å in $\text{LiHC}_2\text{O}_4\cdot\text{H}_2\text{O}$, 1.252 Å in $(\text{CH}_3)\text{NH}_3\text{HC}_2\text{O}_4$ and 1.261 Å in $(\text{CH}_3)_2\text{NH}_2\text{HC}_2\text{O}_4$.

Disorder considerations

The distinct double peaks representing H(4) in the difference synthesis immediately raise the suggestion that the entire oxalate group in HYHOX is disordered. The observed hydrogen oxalate chains would thus be a statistical superposition of two identical chains, each of the lower symmetry type as found in DYDOX and running in opposite directions. It follows that the $\text{O}\cdots\text{O}$ bond in HYHOX would then be seen as a superposition of $\text{O}-\text{H}\cdots\text{O}$ and $\text{O}\cdots\text{H}-\text{O}$. The structure

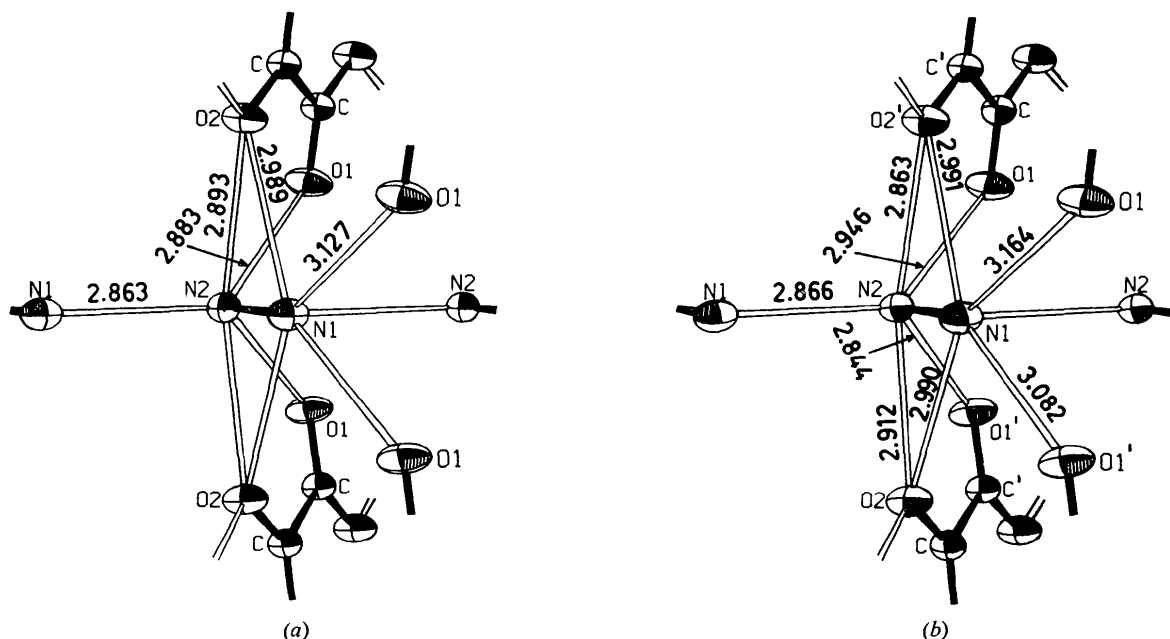


Fig. 3. The hydrogen bond system in: (a) HYHOX and (b) DYDOX. Hydrogen bonds are open.

found for DYDOX could then represent an ordering of this situation in which the DC_2O_4^- chains in adjacent layers (at $y \sim \frac{1}{4}$ and $y \sim \frac{3}{4}$) run in opposite directions.

Whether this extended disorder actually occurs in HYHOX, or whether the disorder affects only the hydrogen atom H(4), is indiscernible from the results of the present study. Two suggestive points tending to favour the more extensive disorder theory do emerge however.

(a) The C_2O_4 group is almost perfectly planar in HYHOX, the dihedral twist about the C-C bond is $0.1(2)^\circ$. The corresponding value in DYDOX is $1.4(2)^\circ$.

(b) The average C and O positions obtained by superposing two DYDOX asymmetric units in the manner suggested above correspond closely with the C and O positions refined for HYHOX (see Table 2).

The isotope effect

In the light of the previous paragraph, it is not possible to say whether the differences observed in the two structures are real or artifacts of disorder. A factor common to both possibilities, however, is the form of the hydrogen atom potential functions for H(4) and

D(4). It has been suggested by Rundle (1964) that the occurrence of an isotope effect (more specifically, a lengthening) in a short symmetric hydrogen bond gives clear indication of a *double*-minimum potential. The absence of a length change can be taken to imply an effectively *single*-minimum potential. Both statements have been shown by Singh & Wood (1969) to have a sound theoretical basis. It would normally be concluded, therefore, that the $\text{O}\cdots\text{H}\cdots\text{O}$ bond in HYHOX is indeed of the symmetric double-minimum potential type. The ground-state vibrational level for H(4) could then be assumed to lie sufficiently high in the (double-minimum) potential well for classical thermally activated jumps or quantum-mechanical tunneling effects to maintain equilibrium between the two troughs in the potential (also see Hamilton & Ibers, 1968). The relevance of such arguments is questionable, however, in view of the large-scale disorder possibility discussed above.

If we accept the argument favouring a symmetric double-minimum potential for H(4), then a possible explanation of the effect of deuteration follows readily: assuming the same general form for the potential for D(4), the ground-state vibrational energy for the deuterium atom will be lower. This means that the condi-

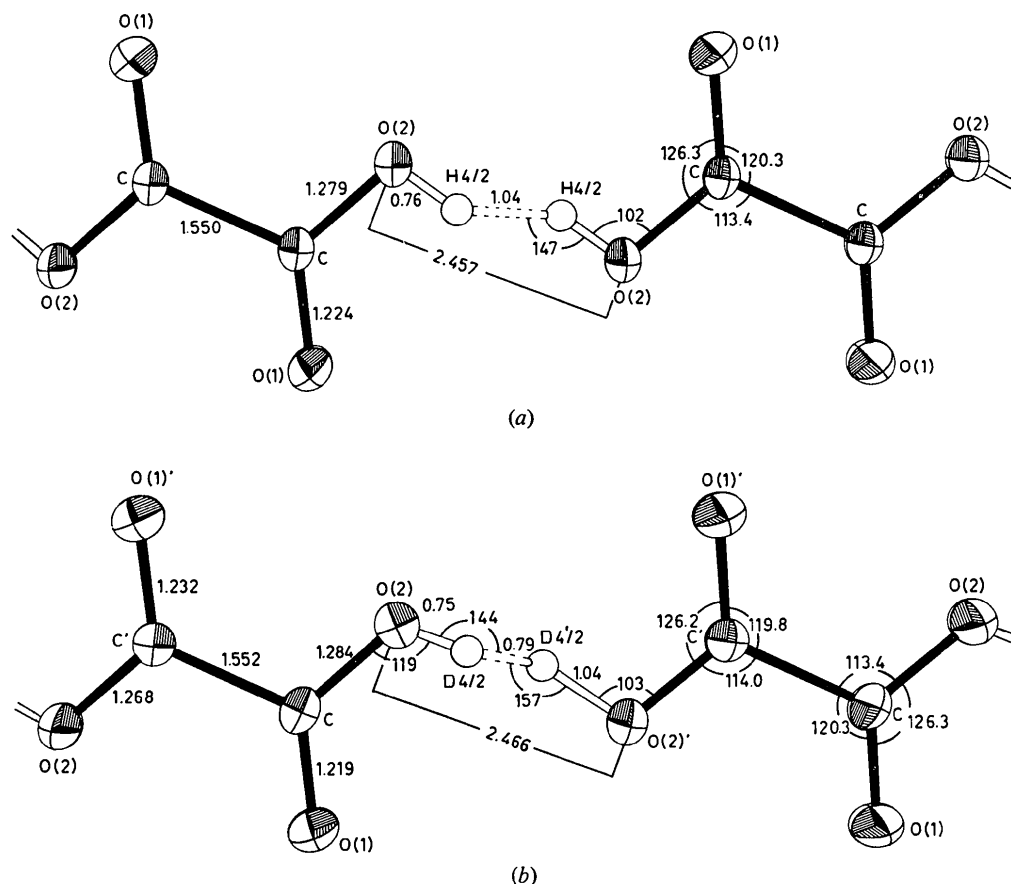


Fig. 4. The final refined models for the hydrogen oxalate chains in: (a) HYHOX and (b) DYDOX.

tions under which D(4) can make jumps or tunnel to the neighbouring trough in the potential become more unfavourable. The efficiency of the mechanism for maintaining dynamical equilibrium between the two troughs of the potential so impeded, the tendency will be for the ordered, lower-symmetry structure to develop. This does not, however, eliminate the possibility of some degree of static disorder being present in the system.

It is clear from this that a reinvestigation of the two structures both above and below room temperature would be most rewarding, as would a systematic calorimetric study.

A final remark is warranted in connexion with the earlier referred to infrared study of Lindgren *et al.* (1969). Evidence was found to suggest that the symmetric $O \cdots H \cdots O$ bond in HYHOX became asymmetric on deuteration, a prediction which is vindicated by the present findings. On the other hand, their suggestion that the potential associated with the $O \cdots H \cdots O$ bond is of the single-minimum type would appear to contradict the conclusions drawn here. It may be that an artificial distinction is here being made, however, between single- and double-minimum potentials. The ground-state vibrational level for the atom H(4) may lie sufficiently near the top of the central peak of a double-minimum potential, that the concept of single- and double-potential minima ceases to be meaningful. This further illustrates the difficulties in analysing this type of structural phenomenon.

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