The maximum difference between the P—O bond lengths of the rings is 0·013 Å (3σ) and the mean length is 1·560 Å. The four C—O, the four C(sp^2)—C(sp^3) and the four C(sp^3)—C(sp^3) bond lengths vary by maximum values of 0·021 (3σ), 0·020 (2σ) and 0·009 (2σ) Å with mean lengths of 1·458, 1·523 and 1·527 Å respectively. The C—H bond lengths vary by a maximum of 0·375 Å (9σ) with a mean length of 1·07 Å. The P(2)—O(120) and P(12)—O(12) bond lengths are identical within the observed error with a mean value 1·47 Å. Only the P(2)—S(2) = 1·871 (5) and P(12)—S(20) = 1·78 (3) Å bonds are distinctly different, being shorter than in other organic thiophosphates. In other structures the length of this bond varies from 1·884 to 1·942 Å (Wieczorek, Sheldrick, Karolak-Wojciechowska, Mikołajczyk &

Ziemnicka, 1979; Wieczorek, Karolak-Wojcie-chowska, Mikołajczyk & Witczak, 1978). The shortening of these bonds could be partly due to the difficulty in the refinement of the disordered and partially overlapping atoms S(20) and O(12), and S(2) and O(120).

The molecular packing (Fig. 4) shows a distinct shortening of the S(20)—H and S(2)—H intermolecular distances.

Fig. 4. The molecular packing, showing some intermolecular distances (Å).

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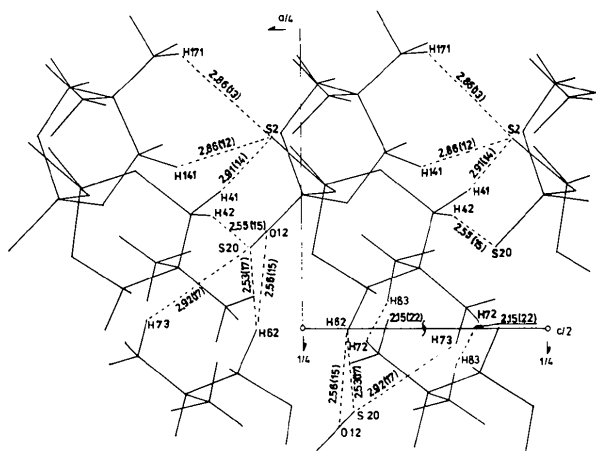

Neutron Diffraction Study of 2-Nitro-1,3-indandione Dihydrate*

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Abstract. $H_5O_2^+.C_9H_4NO_4^-$, monoclinic, $P2_1/c$, $Z = 4$, $a = 9·633$ (1), $b = 5·176$ (1), $c = 19·713$ (2) Å, $\beta = 102·59$ (1)°; neutron wavelength 1·210 Å, μ(measured) = 0·158 mm^{-1}. Refinement with 2652 data recorded at 294 K gave a final $R_w(F^2) = 0·050$. The $H_5O_2^+$ complex is an aquaoxonium ion, $H_3O^+.H_2O$. The O$\cdots$O distance in the internal H bond is 2·477 (2) Å; the O—H and H$\cdots$O distances are 1·087 (3) and 1·390 (3) Å respectively. The $H_5O_2^+$ complex is H bonded to O in four different nitronate ions. One of the water H atoms participates in a bifurcated H bond.

Introduction. An earlier X-ray study of the dihydrate of 2-nitro-1,3-indandione indicated the presence of the hydrated proton complex $H_5O_2^+$ (Simonsen & Jacobsen, 1977). The $H_5O_2^+$ complex is here isolated, which should be taken to mean that the complex is not H bonded to other such complexes or to water molecules. An interesting and important feature in the geometry of the $H_5O_2^+$ ion is the location of the proton in the short internal H bond. If the H atom is at, or very near, the centre of the bond, the complex is best described as a diaquahydrogen ion. When the H atom is near one of the two water molecules, it is described as an aquaoxonium ion. In both cases the overall formula $H_5O_2^+$ may be justified as a means of describing the structural units (Lundgren & Olovsson, 1976). The $O{\cdots}O$ distance of 2·507 (5) Å for the H bond in the present compound, as reported by Simonsen & Jacobsen (1977), is larger than the average value, 2·44 Å, found in fifteen structure determinations of $H_5O_2^+$ complexes (Lundgren & Olovsson, 1976). It may be that the present compound provides a case where the $H_5O_2^+$ complex is an aquaoxonium ion, $H_3O^+.H_2O$.

Crystals of the dihydrate were grown from an aqueous solution of 2-nitro-1,3-indandione. Cell dimensions were determined from the measured θ values of 32 reflexions recorded on a powder photograph taken with a Guinier–Hägg focusing camera at 295 K, monochromatized Cr $K\alpha_1$ radiation ($\lambda = 2\cdot28975$ Å) and CoP_3 ($a = 7\cdot70778$ Å) as an internal standard. The refined cell dimensions deviate from those reported by Simonsen & Jacobsen (1977) by up to 1·3% (see also Simonsen & Jacobsen, 1978).

A plate-shaped crystal with a volume of 29·3 mm³ was used for data collection. Neutron intensities for 2654 independent reflexions up to sin $\theta/\lambda = 0\cdot69$ Å^{-1} were recorded at 294 K with an ω–2θ step-scan technique on a Hilger & Watts computer-controlled four-circle diffractometer at the Swedish Atomic Energy R2 reactor at Studsvik. Three test reflexions were monitored regularly, but no systematic changes in their intensities were observed. The data were corrected for Lorentz and absorption effects. The transmission factors were in the range 0·567–0·836. Variances assigned to the intensities were based on Poisson counting statistics and the scatter observed in the test reflexions (McCandlish, Stout & Andrews, 1975).

The H atoms were located from a difference synthesis based on non-hydrogen parameters from the X-ray study. Least-squares refinement minimizing $\sum w(F_o^2 - k^2 F_c^2)^2$, where $w^{-1} = \sigma^2(F_o^2)$, included 227 parameters: one scale factor, an isotropic extinction parameter, positional and anisotropic thermal parameters for the 25 independent atoms. The final $R(F^2) = \sum |F_o^2 - F_c^2|/\sum F_o^2 = 0\cdot053$ and $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w F_o^4]^{1/2} = 0\cdot050$. The standard deviation of an observation of unit weight, s, was 1·04. A δR plot of the data is shown in Fig. 1 (Abrahams & Keve, 1971).

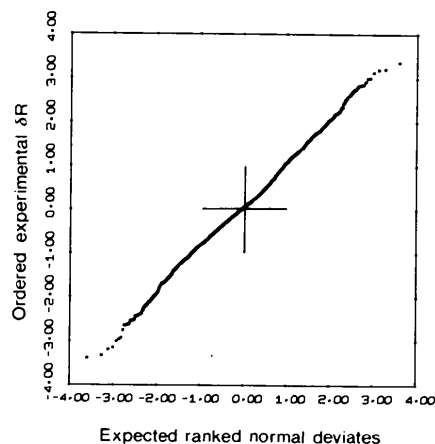Fig. 1. A δR plot of the data after the last cycle of refinement. The slope of the least-squares line through the points is 0·96, and the y intercept is 0·08. The points for three reflexions are outside the plot range.

The refined value of the isotropic extinction factor, g, was 3·28 (10) × 10³ (Coppens & Hamilton, 1970). 25 reflexions suffered an intensity loss >15% due to extinction, with a maximum value of 57%. Coherent scattering amplitudes were taken from Bacon (1974). Final positional parameters are given in Table 1.* The

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35552 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^5$)

U_{eq} is the geometric mean of the r.m.s. components of thermal displacement along the principal axes ($\times 10^3$)

	x	y	z	U_{eq} (Å^2)
C(1)	36955 (7)	7302 (16)	36834 (3)	163 (2)
C(2)	28133 (8)	6437 (16)	41901 (3)	165 (2)
C(3)	17192 (7)	26160 (17)	40366 (4)	165 (2)
C(3a)	19628 (7)	40009 (16)	34077 (3)	161 (2)
C(4)	12420 (8)	60672 (18)	30442 (4)	174 (2)
C(5)	16748 (9)	68921 (18)	24470 (4)	188 (2)
C(6)	27926 (9)	56866 (19)	22245 (4)	191 (2)
C(7)	35314 (8)	36426 (18)	26007 (4)	183 (2)
C(7a)	31014 (7)	28399 (16)	31917 (4)	165 (2)
O(1)	47279 (10)	−5736 (22)	36290 (5)	185 (3)
O(3)	7599 (11)	30760 (24)	43392 (5)	192 (3)
O(4)	39161 (11)	−27979 (23)	47868 (5)	193 (3)
O(5)	21134 (12)	−11310 (24)	51147 (6)	204 (4)
N(2)	29420 (6)	−11294 (12)	47158 (3)	175 (2)
H(4)	3700 (19)	70113 (42)	32147 (11)	222 (5)
H(5)	11356 (23)	85006 (47)	21494 (12)	240 (6)
H(6)	30977 (24)	63500 (50)	17569 (11)	241 (6)
H(7)	44115 (22)	27284 (47)	24326 (11)	232 (6)
O(w1)	62815 (14)	−44643 (26)	41062 (6)	206 (3)
O(w2)	87710 (13)	−31302 (30)	41553 (7)	206 (4)
H(11)	55916 (20)	−29770 (43)	40068 (10)	225 (5)
H(12)	61838 (22)	−54592 (44)	45261 (11)	234 (5)
H(13)	73772 (26)	−38908 (44)	41306 (10)	232 (5)
H(21)	94683 (23)	−45089 (50)	42271 (10)	235 (5)
H(22)	90050 (29)	−20528 (63)	45508 (17)	278 (7)

programs used for all calculations on IBM 370/155, IBM 1800 and NORD-100 computers have been described by Lundgren (1979).

Discussion. The structure is composed of 1,3-indandione-2-nitronate ions H bonded *via* $H_5O_2^+$ complexes to form double layers parallel to the *ab* plane (Fig. 2). Distances and angles involving non-hydrogen atoms agree within 3σ (0·018 Å, 0·5°) with the corresponding values calculated from the coordinates of Simonsen & Jacobsen (1977) and our cell parameters. The dimensions of the nitronate ion are shown in Fig. 3.
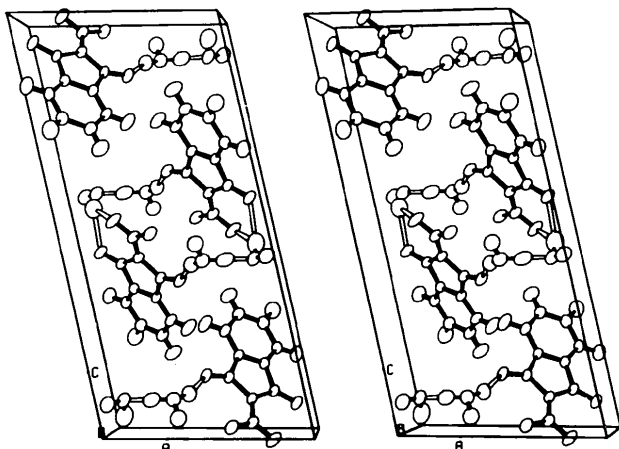

Fig. 2. Stereoscopic *ORTEP* drawing (Johnson, 1965) of the crystal structure of 2-nitro-1,3-indandione dihydrate. Covalent bonds are filled and H bonds are open. Thermal ellipsoids are scaled to enclose 50% probability.
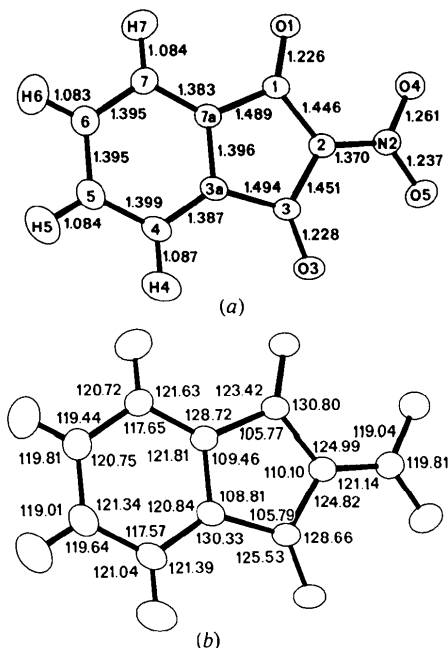

(a)

(b)

Fig. 3. (a) Bond distances (Å) and (b) angles (°) in the nitronate ion. E.s.d.'s of C—H distances are 0·002–0·003 Å and for other distances 0·001 Å. E.s.d.'s of angles involving H are 0·14–0·16° and for other angles 0·06–0·09°.

A rigid-bond test (Hirshfeld, 1976) applied to the bonds in the nitronate ion indicates that the thermal parameters obtained in the refinement are reasonable. The quantities $Z_A^2 - Z_B^2$, where Z_A^2 is the mean-square amplitude of vibration of atom A along the bond $A-B$ and Z_B^2 is the mean-square amplitude of B along $B-A$, are in the range 0·0001–0·0014 Å² for the 15 bonds not involving H, with an average of 0·00059 Å². The average value for C—H is 0·0057 Å². The deviations from planarity and twofold symmetry (Table 2 and Fig. 3) of the nitronate ion may be explained by the intermolecular bonding. N—O(5) is significantly shorter than N—O(4), which may be explained by the fact that O(5) is one of the acceptors of a weak bifurcated bond (Fig. 4), whereas O(4) participates in a normal linear H bond.

The geometry of the $H_5O_2^+$ complex is given in Table 3 and Fig. 4. The internal O···O bond is the longest found when the geometry has been determined by neutron diffraction (Table 4). The complex is clearly an aquaoxonium ion, with a normal H_2O molecule bonded to a distorted H_3O^+ ion. The H_3O^+ ion is pyramidal; the O atom is situated 0·29 Å from the plane defined by
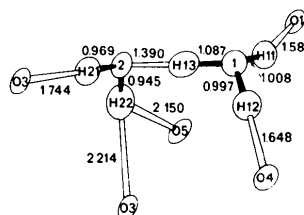

Fig. 4. Bond distances (Å) in the $H_5O_2^+$ complex.

Table 2. *Distances of atoms* (Å) *from the least-squares plane*

The plane is defined by atoms C(3a), C(4), C(5), C(6), C(7) and C(7a). The equation of the plane is $-5·121x - 3·327y - 8·326z + 5·184 = 0$. The NO₂ group is twisted 4·89° to the least-squares plane.

C(1)	−0·019 (1)	C(6)	0·009 (1)	O(4)	0·124 (1)
C(2)	0·040 (1)	C(7)	−0·002 (1)	O(5)	0·219 (1)
C(3)	0·072 (1)	C(7a)	−0·007 (1)	H(4)	−0·015 (2)
C(3a)	0·010 (1)	N(2)	0·126 (1)	H(5)	−0·016 (2)
C(4)	−0·006 (1)	O(1)	−0·068 (1)	H(6)	0·022 (2)
C(5)	−0·005 (1)	O(3)	0·158 (1)	H(7)	−0·009 (2)

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°)

X	H	Y	X–H	H···Y	X···Y	$\angle X$–H···Y
O(w1)–H(11)···O(1)			1·008 (3)	1·589 (2)	2·563 (2)	160·9 (2)
O(w1)–H(12)···O(4)			0·997 (3)	1·648 (3)	2·643 (2)	177·2 (2)
O(w1)–H(13)···O(w2)			1·087 (3)	1·390 (3)	2·477 (2)	179·2 (2)
O(w2)–H(21)···O(3)			0·969 (3)	1·744 (3)	2·712 (2)	177·9 (2)
O(w2)–H(22)···O(3)			0·945 (4)	2·214 (4)	2·903 (2)	129·0 (3)
O(w2)–H(22)···O(5)			0·945 (4)	2·150 (3)	2·863 (2)	131·3 (3)
H(11)–O(w1)–H(12)			112·2 (2)	H(21)–O(w2)–H(22)		106·3 (3)
H(11)–O(w1)–H(13)			113·1 (2)	H(13)···O(w2)–H(21)		115·5 (2)
H(12)–O(w1)–H(13)			111·8 (2)	H(13)···O(w2)–H(22)		104·5 (2)

Table 4. *Geometry of the internal* H *bond of* $H_5O_2^+$ *as determined by neutron diffraction*

Compound	Symmetry at bond centre	O···O (Å)	O–H (Å)	H···O (Å)	O–H···O (°)	Reference
o-C$_6$H$_4$(COOH)SO$_3$H.3H$_2$O	–	2·414 (3)	1·201 (5)	1·219 (5)	172·5 (3)	Attig & Williams (1976)
Co(en$_2$)Cl$_3$.HCl.2H$_2$O	$\bar{1}$	2·431 (6)	1·215		180	Rozière & Williams (1976)
C$_6$H$_2$(NO$_2$)$_3$SO$_3$H.4H$_2$O	–	2·436 (2)	1·128 (4)	1·310 (4)	175·0 (3)	Lundgren & Tellgren (1974)
C$_6$H$_3$(COOD)(OD)SO$_3$D.2D$_2$O	$\begin{cases} \bar{1} \\ \bar{1} \end{cases}$	2·435 (3) 2·442 (3)	1·217 1·221		180 180	Attig & Williams (1977)
YH(C$_2$O$_4$)$_2$.3H$_2$O	2	2·442 (2)	1·221		178·2 (3)	Brunton & Johnson (1975)
C$_9$H$_5$O$_2$NO$_2$.2H$_2$O	–	2·477 (2)	1·087 (3)	1·390 (3)	179·2 (2)	This work

H(11), H(12) and H(13). The long O–H distance, 1·087 (3) Å, and the short O···O distance, 2·477 (2) Å, fit well into the plot of O–H *vs* O···O distances given by Olovsson & Jönsson (1976). $Z^2_{H(13)} - Z^2_{O(w1)}$ is large, 0·0277 Å^2, in accordance with a broad, flat potential well. The corresponding values for the remaining four H atoms of the $H_5O_2^+$ complex are 0·0086, 0·0128, 0·0088 and 0·0069 Å^2 for H(11), H(12), H(21) and H(22) respectively. The conformation of the $H_5O_2^+$ complex is *gauche*. The angle between the planes defined by the central O···O bond and the bisectors of the outer H–O–H angles is 60·7°.

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Structure of DL-α-Amino-*n*-butyric Acid (Modification *A*): A Reinvestigation

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Abstract. C$_4$H$_9$NO$_2$, monoclinic, $P2_1/a$, $a = 9\cdot829$ (4), $b = 4\cdot78$ (2), $c = 11\cdot908$ (5) Å, $\beta = 101\cdot02$ (4)°, $V = 549\cdot2$ Å^3, $Z = 4$, $D_c = 1\cdot247$ Mg m^{-3}. Modification *A* shows disorder with regard to the position of the terminal methyl group. The structure was refined both with and without constraints for the geometry of this terminal methyl group, and yielded final *R* values of 0·052 and 0·077, respectively, for 675 reflexions.