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The Crystal Molecular Structure of 2-Nitro-1,3-indandiol

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The crystal structure of $C_9H_9NO_4$, 2-nitro-1,3-indandiol, has been determined by X-ray diffraction analysis, using Mo$K\alpha$-radiation. The space group is $I4_1/a$ (no. 88), with cell dimensions a=19.8402(9) Å and c 8.7315(4) Å. Least squares refinement with 4799 observed reflections converged at R=0.0437 and S=2.59. The average e.s.d. in bonding distances is 0.0009 Å for bonds not involving hydrogen atoms. The molecule has small but significant deviations from molecular mirror symmetry, caused by the hydrogen bonding arrangement, which comprises two O–H···O bonds and two C–H···O bonds. The molecular configuration is *trans-trans*.

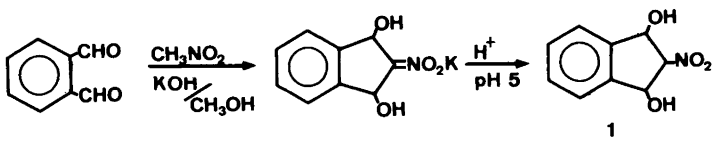
In connection with work aimed at the production of possible precursors in the synthesis of isoindenes, *cis*-1,3-indandiols with various substituents in the 2-position were required. The reaction between phthalaldehyde and nitromethane in ethanolic potassium hydroxide was found to be a convenient starting point as it provides a high yield of the 2-nitronate of 1,3-indandiol from which 2-nitro-1,3-indandiol (*1*) is obtained by careful protonation [Scheme 1; eqn. (1)].[1] The nitro group in *1* is excellently suited for introduction of other substituents in the 2-position.

Theoretically there are four stereoisomers of *1*; *cis-cis, trans-trans,* and two enantiomeric *cis-trans* stereoisomers. According to Angyall and Lutrell,[2] the protonation of nitronates flanked by hydroxyl groups is a thermodynamically controlled process where the *trans-trans* isomer predominates among the products. As far as we know, this has never been unambiguously demonstrated for the 2-nitro-1,3-indandiol system.

Routine ^{1}H NMR measurements could not give a unique answer, and an X-ray diffraction analysis was carried out, primarily to establish the stereochemistry of *1*. There are, however, additional interesting aspects of this structure. In the related 2-nitro-1,3-indandione[3] the C(2) proton is completely transferred to water of crystallization, and although *1* is a considerably weaker carbon acid, it may be a likely candidate to have C(2)–H···O hydrogen bonds in the crystal. The crystallographic evidence for such interactions is, according to Taylor and Kennard,[4] "sparse and circumstantial".

If the product is the *cis-cis* isomer there may be strong intramolecular hydrogen bonds or other intramolecular interactions of general interest. The free molecule should have mirror symmetry in the *cis-cis* and *trans-trans* isomers. If this assumed symmetry is not utilized as a part of the space group symmetry, the influence of crystal field asymmetries on the molecular structure may be observed.

This work is mainly a presentation of the crystallographic results, and only a brief account of the NMR results will be given.



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Scheme 1. Eqn. (1).

0302-4369/84 $2.50

EXPERIMENTAL

^{1}H NMR measurements were performed in CD_3CN solution on a 60 MHz Varian spectrometer. The spectrum has a 4H singlet at δ=7.3 ppm, a 2H triplet at 5.4, a 1H triplet at 4.8 and a 2H doublet at 4.4 ppm, later assigned to the aromatic protons, the 1,3-protons, the 2-proton and the hydroxyl protons, respectively. Coincidental coupling constants of 7.5 Hz between the 1,3-protons and the 2-proton and between the 1,3-protons and the hydroxyl protons account for this unexpected pattern. By deuterium exchange of the hydroxyl protons the coupling pattern was simplified in the expected way as the doublet at 4.4 ppm disappeared and the triplet at 5.4 ppm changed to a doublet. From the remaining A_2X spectrum the vicinal coupling constant was determined to be 7.5 Hz.

Well developed, slightly brownish crystals were grown by evaporation from a solution of ethyl acetate and petroleum ether. The melting point was 166–168 °C (lit.[1] 166–168 °C). An approximately equilateral parallelepiped with dimensions 0.3×0.3×0.3 mm was used throughout the X-ray measurements. The tetragonal space group was found to be $I4_1/a$ (no. 88) with reflection conditions: (hkl): $h+k+l=2n$; $(hk0)$:$h=2n$; and (001):$l=4n$. The cell dimensions were determined from a least-squares fit to 2θ-values for 26 reflections. Crystal data, at T=130 K, are: a=19.8402(9) Å, c=8.7315(4) Å, V=3437.0 Å^3, Z=16, D_x=1.509 g cm^{-3}, $F(000)$=1632, and μ=1.127 cm^{-1}.

Intensity data were collected with the crystal kept at approximately 130 K on an automatic SYNTEX P$\bar{1}$ diffractometer using graphite monochromated Mo$K\alpha$-radiation (λ=0.71069 Å). The data set was recorded in two parts. All 2678 unique reflections with $2\theta<60°$ were measured. 2342 have been treated as observed ($I>3\sigma(I)$). For $60°<2\theta<90°$ only reflections with intensity larger than a preset threshold value were measured, thus giving 2457 observed reflections in this region. The experimental stability was checked by periodic measurements of three test reflections, and the reproducibility was further checked by comparison with a small pre-collected data set in the interval $25°<2\theta<30°$. Further data about the stability check and this comparison are available from the authors. A normal probability plot[5] from this comparison using e.s.d.'s from counting statistics alone (assuming the scale factor between the two sets to be 1) reveals a small systematic difference and an average underestimation of the e.s.d.'s of about 25 %. The systematic difference is consistent with a noticeable decrease in the test reflection intensities of about 1.5 % during the experiment. Although neither the systematic difference between the two sets nor the decrease in test reflections intensities are significant (both being about 1σ), the decrease was corrected for. The random variation of the test reflections, not accounted for by the counting statistics, was less than 1 %,* nevertheless a value of 1.5 % was used to calculate the e.s.d.'s of the intensities. A new normal probability plot with the same data indicates that this is an overestimation of about 25 % of the e.s.d.'s. This is clearly allowable in view of the neglect of absorption, extinction, TDS and truncation corrections, and, with respect to the least-squares refinement weighting function, the use of the free atom model.

The data were converted to structural amplitudes in the conventional way using programs locally adapted to a CYBER-76 computer.[6]

Absorption correction was not deemed necessary.

STRUCTURE DETERMINATION AND REFINEMENT

The phase problem was straightforwardly solved by direct methods,[7] and after a few cycles of least-squares refinement[6,8] (the last one using anisotropic thermal parameters) all hydrogen atoms were located from a difference Fourier map. The least-squares refinement with all 4799 observed reflections, including positional parameters for all atoms, anisotropic thermal parameters for non-hydrogen atoms, isotropic thermal parameters for hydrogen atoms and a scale factor (163 variable parameters) converged with a conventional R=0.0369, R_w=0.0437 and goodness-of-fit, S=2.59. A high-angle refinement using only reflections with $\sin\theta/\lambda>0.7$ Å^{-1} (2489 observations) and fixed hydrogen atom parameters terminated at R=0.0309 (R_{total}=0.0389), R_w=0.0298 and S=1.096. In spite of the 50 % reduction in the number of observations, the e.s.d.'s in the atomic parameters are considerably lower for the high-angle refinement. Final coordinates from the refinement using all data are given in Table 1, together with the equivalent B-values[9], whereas the results from the high-angle refinement are available from the authors.

* Calculated as $\left(\frac{\sigma^2_{obs}-\sigma^2_{count}}{\bar{I}^2}\right)^{\frac{1}{2}} \cdot 100$ %, where $\sigma^2_{obs}=\frac{1}{n-1}\sum_{i=1}^{n}(I_i-\bar{I})^2$.

Table 1. Atomic coordinates and B_{eq}/B_{iso} as obtained from the refinement using all data. E.s.d. in last digit is given in parenthesis. B_{eq} is calculated as $B_{eq}=\frac{1}{3}\sum_{i=1}^{3}B_{ii}$.

Atom	*X*	*Y*	*Z*	*B*
C(1)	0.12254(3)	0.52058(3)	0.67525(7)	0.890(10)
C(2)	0.11014(3)	0.56658(3)	0.81582(7)	0.918(10)
C(3)	0.03847(3)	0.59450(3)	0.79660(8)	0.918(10)
C(4)	0.03188(3)	0.59687(3)	0.62448(8)	0.926(10)
C(5)	−0.01531(3)	0.63161(4)	0.53756(8)	1.146(12)
C(6)	−0.01412(4)	0.62304(4)	0.37889(9)	1.246(12)
C(7)	0.03294(4)	0.58039(4)	0.31037(8)	1.221(12)
C(8)	0.08029(4)	0.54544(4)	0.39789(8)	1.111(12)
C(9)	0.07914(3)	0.55432(3)	0.55598(8)	0.924(10)
N(2)	0.11723(3)	0.52991(3)	0.96481(7)	1.211(11)
O(1)	0.19120(2)	0.51749(3)	0.62964(6)	1.032(9)
O(3)	0.03279(3)	0.65728(3)	0.87528(7)	1.303(10)
O(4)	0.15885(3)	0.55039(4)	1.05714(7)	1.875(14)
O(5)	0.08009(3)	0.48123(3)	0.98641(7)	1.716(12)
H(1)	0.1073(5)	0.4744(5)	0.6959(11)	0.87(18)
H(2)	0.1412(5)	0.6024(5)	0.8185(10)	0.79(17)
H(3)	0.0056(5)	0.5647(5)	0.8371(11)	0.82(18)
H(5)	−0.0469(5)	0.6602(5)	0.5867(12)	1.49(20)
H(6)	−0.0434(5)	0.6467(5)	0.3153(12)	1.60(21)
H(7)	0.0323(5)	0.5748(5)	0.1984(13)	1.72(21)
H(8)	0.1122(5)	0.5172(5)	0.3494(13)	1.62(21)
H(01)	0.2132(7)	0.4921(7)	0.6883(15)	3.12(28)
H(03)	−0.0070(8)	0.6703(7)	0.8809(17)	3.89(31)

Lists of structure amplitudes, observed and calculated, e.s.d. of the observations, anisotropic thermal parameters, data for thermal motion analysis, a full list of torsional angles and least squares planes equations are available from the authors. Owing to the neglect of absorption, extinction, TDS and truncation corrections, the thermal parameters are expected to be biased, and conclusions based on their absolute values thus of reduced significance. Nevertheless, an analysis of the thermal parameters has been performed,[10] and the thermal motion found is reasonably well approximated by a rigid body model.

The rigid bond test of Hirshfeld[11] was satisfactory, except for the N−O bonds, indicating that the relative thermal motion is reasonably well described. The average libration correction of the bonding distances resulting from the rigid body model is 0.0016 Å, with a root-mean-square deviation of 0.0003 Å.

The molecule is shown in Fig. 1, with thermal ellipsoids scaled to include 50 % probability, atomic notation and the dihedral angles relevant to the NMR measurements. Fig. 2 displays the crystal packing with hydrogen bonds as derived from the refinement using all data. Tables 2−5 give several derived molecular structural parameters, whereas Table 6 gives hydrogen bond parameters corresponding to the high-angle refinement with normalized X−H bond distances, as recommended by Kennard and Taylor.[12]

DISCUSSION

As previously mentioned the NMR spectra could not give a unique answer with respect to the stereochemistry of the title compound. The simplicity of the spectra could, however, exclude the two *cis-trans* isomers. Application of the Karplus rules to the observed coupling constant of 7.5 Hz gave two possible dihedral angles between the vicinal 1,3- and 2-protons,[13] 19°

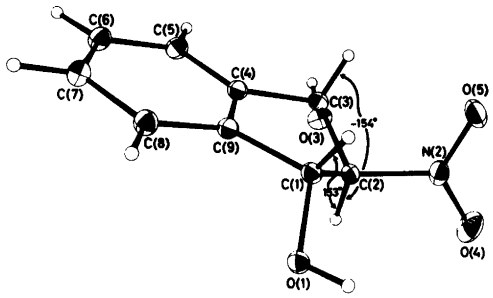

Fig. 1. Perspective drawing of the 2-nitro-1,3-indandiol molecule[14], including thermal ellipsoids scaled to include 50 % probability, atomic notation, and the dihedral angles relevant to the NMR measurements.

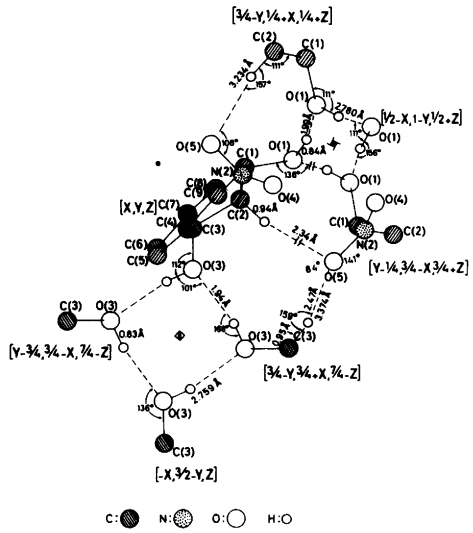

Fig. 2. The hydrogen bonding in 2-nitro-1,3-indandiol. The view is towards the *c*-axis, with the *b*-axis pointing to the right and the *a*-axis pointing down. Parameters of the hydrogen bonds, as derived from the refinement using all data are given.

corresponding to the *cis-cis* isomer, and 152° corresponding to the *trans-trans* isomer. The X-ray work unambiguously shows that the *trans-trans* isomer is the product of the synthesis briefly described in the introduction (eqn. 1) The almost exact correspondanee of the dihedral angles as measured by NMR in solution and by X-ray diffraction in the solid state (Fig. 1), may be an indication of negligible conformational perturbations on the molecule (apart from rotation of the hydroxyl and nitro groups) upon solidification.

The conformation of the molecule is as expected with an almost planar carbon framework, excepting C(2) which is out of the plane in such a

Table 2. Bond distances in 2-nitro-1,3-indandiol. The three columns give values derived from: I, refinement using all data; II, refinement using only high angle data ($\sin\theta/\lambda > 0.7$ Å^{-1}); and III, as II, but corrected for libration. Distances are given in Å, with e.s.d.'s in the last digit in parenthesis. The average C–H distance is 0.95 with an average e.s.d. of 0.01 Å, compared to a sample e.s.d. of 0.022 Å.

Bond	I	II	III
C(1)–C(2)	1.5492(9)	1.5507(7)	1.5526
C(1)–C(9)	1.5080(9)	1.5103(7)	1.5119
C(2)–C(3)	1.5353(9)	1.5357(9)	1.5371
C(3)–C(4)	1.5092(9)	1.5111(8)	1.5129
C(4)–C(9)	1.3963(9)	1.3949(7)	1.3963
C(4)–C(5)	1.3884(9)	1.3923(8)	1.3936
C(5)–C(6)	1.3960(10)	1.3968(10)	1.3985
C(6)–C(7)	1.3948(10)	1.3999(10)	1.4013
C(7)–C(8)	1.3955(10)	1.3985(9)	1.3999
C(8)–C(9)	1.3918(10)	1.3930(8)	1.3947
C(1)–O(1)	1.4204(8)	1.4160(7)	1.4174
C(3)–O(3)	1.4270(8)	1.4231(7)	1.4249
C(2)–N(2)	1.4972(9)	1.4943(7)	1.4960
N(2)–O(4)	1.2234(9)	1.2244(9)	1.2260
N(2)–O(5)	1.2293(9)	1.2292(9)	1.2309

Table 3. Bond angles in 2-nitro-1,3-indandiol. Columns I and II are as in Table 2, and the values are given in degrees with e.s.d.'s in last digit in parentheses.

Angle	I	II	Angle	
C(2)–C(1)–C(9)	101.24(5)	101.17(4)	C(2)–C(1)–H	101.8(6)
C(2)–C(1)–O(1)	113.56(5)	113.71(4)	C(9)–C(1)–H	111.4(6)
C(9)–C(1)–O(1)	111.91(5)	112.09(4)	O(1)–C(1)–H	107.9(6)
C(1)–C(2)–C(3)	105.84(5)	105.97(4)	C(1)–C(2)–H	111.2(6)
C(1)–C(2)–N(2)	112.78(5)	112.91(4)	C(3)–C(2)–H	109.7(6)
C(3)–C(2)–N(2)	110.94(5)	111.00(4)	N(2)–C(2)–H	106.5(6)
C(2)–C(3)–C(4)	101.55(5)	101.52(4)	C(2)–C(3)–H	111.8(6)
C(2)–C(3)–O(3)	109.60(5)	109.80(4)	C(4)–C(3)–H	109.3(6)
C(4)–C(3)–O(3)	116.46(6)	116.43(5)	O(3)–C(3)–H	108.0(6)
C(3)–C(4)–C(5)	128.18(6)	128.02(5)		
C(3)–C(4)–C(9)	110.46(6)	110.55(4)	C(4)–C(5)–H	119.8(6)
C(5)–C(4)–C(9)	121.25(6)	121.34(6)	C(6)–C(5)–H	122.2(6)
C(1)–C(9)–C(8)	128.27(6)	128.09(5)	C(5)–C(6)–H	121.4(7)
C(1)–C(9)–C(4)	110.86(6)	110.91(4)	C(7)–C(6)–H	117.9(7)
C(8)–C(9)–C(4)	120.83(5)	120.95(5)		
			C(6)–C(7)–H	119.1(6)
C(4)–C(5)–C(6)	118.06(6)	117.97(5)	C(8)–C(7)–H	119.8(6)
C(5)–C(6)–C(7)	120.72(6)	120.77(5)		
C(6)–C(7)–C(8)	121.14(7)	121.04(5)	C(7)–C(8)–H	120.0(7)
C(7)–C(8)–C(9)	117.98(6)	117.94(5)	C(9)–C(8)–H	122.0(7)
C(2)–N(2)–O(4)	118.33(7)	118.52(7)	C(1)–O(1)–H	110.7(9)
C(2)–N(2)–O(5)	117.30(6)	117.29(6)	C(3)–O(3)–H	112.0(10)
O(4)–N(2)–O(5)	124.37(7)	124.19(7)		

Table 4. Deviations from least-squares planes through selected parts of the molecule. Plane equations and interplanar angles are available from the authors. Atoms defining the planes are marked with an asterisk behind the calculated deviations. The values are given in Å.

Atom	Plane I	Plane II	Plane III	Plane IV
C(1)	−0.054	−1.216	0.0032*	0.0000*
C(2)	—	0.0010*	0.491	0.0000*
C(3)	−0.082	1.244	−0.0032*	0.0000*
C(4)	0.0002*	—	0.0057*	0.752
C(5)	−0.0018*	—	−0.048	—
C(6)	0.0022*	—	—	—
C(7)	−0.0010*	—	—	—
C(8)	−0.0006*	—	−0.072	—
C(9)	0.0010*	—	−0.0057*	0.738
N(2)	—	−0.0031*	−0.021	−1.177
O(1)	—	—	0.855	0.650
O(3)	—	—	0.845	0.583
O(4)	—	0.0010*	—	—
O(5)	—	0.0010*	—	—
H(2)	—	0.013	—	0.768

Table 5. Torsion angles relevant to the conformation of the substituted part of the molecule. The two columns give values for each of the two halves related through the assumed molecular mirror symmetry. The atoms are labeled with two indices when appropriate. The first index refers to colum 1 and the second to column 2. The values are given in degrees and they are derived from the refinement with high-angle data only. E.s.d.'s are less than 1 in the last digit given.

Torsion angle	1	2
O(1,3)–C(1,3)–C(2)–N(2)	−88.3	83.0
O(1,3)–C(1,3)–C(2)–C(3,1)	150.0	−154.1
O(1,3)–C(1,3)–C(2)–H(2)	31	−34
O(1,3)–C(1,3)–C(9,4)–C(4,9)	−139.4	138.9
O(1,3)–C(1,3)–C(9,4)–C(8,5)	43.1	−44.7
H–O(1,3)–C(1,3)–C(2)	77	−170
H–O(1,3)–C(1,3)–C(9,4)	−169	76
H–O(1,3)–C(1,3)–H(1,3)	−46	−47
N(2)–C(2)–C(1,3)–C(9,4)	151,4	−153.3
O(5)–N(2)–C(2)–C(1,3)	−59.1	59.8
O(4)–N(2)–C(2)–C(1,3)	121.4	−119.8

Table 6. Details of the hydrogen bonding. The non-hydrogen atoms positions are from the high angle data refinement. Hydrogen atom positions are based on normalized X–H bond distances along the X–H directions found. Values are given in Å and degrees. Symmetry codes are given in Fig. 2.

D–H···A	D–H	H···A	D···A	∠D–H···A	∠H···A–X
O(1)–H···O(1)	0.97	1.87	2.778	155	135
O(3)–H···O(3)	0.97	1.80	2.757	167	135
C(2)–H···O(5)	1.10	2.20	3.233	156	109
C(3)–H···O(5)	1.10	2.32	3.370	158	142

way that the nitro group occupies an equatorial position. The deviations from the ideal conformation are significant only in a statistical sense. The plane defined by C(1), C(9), C(4) and C(3) forms an angle of 3° with that of the benzene ring, the angle between the C(1), C(2), C(3) plane and the benzene plane is 29° and the angle between the nitro group plane and the benzene plane is 91°. The torsion angles about the two C–O bonds are not equal, which is to be expected because of the different hydrogen bonding involvement. All other torsion angles are consistent with the assumed mirror symmetry of the molecule within ±1°.

The bonding distances in Table 2 show that the asphericity errors[15] in the positional parameters obtained using all data are small. There is, however, a significant shrinkage of the benzene ring and a lengthening of C–O bonds. The asphericity shifts are in general close to the directions expected from simple bonding theory.

The planar part of the carbon framework has bond distances consistent with the assumed symmetry. The average difference is about 0.9σ. The average difference between the angles related in the same way is about 3.4σ, none of the differences being larger than 0.4°. The hybridizational perturbations on C(4) and C(9), due to the strained connection between the two rings, causes C(4)–C(5) and C(9)–C(8) – and possibly C(4)–C(9) – to be somewhat shorter than the other C–C bonds of the benzene ring. The same effect may be seen in 2-nitro-1,3-indandione.[3]

The substituted part of the molecule does not have the assumed mirror symmetry. C(1)–C(2) is 0.015 Å longer than C(3)–C(2), and C(1)–O(1) is 0.007 Å shorter than C(3)–O(3). The latter difference may, in part, be a result (by

conjugation) of the former. This asymmetry, as well as the difference between the two N–O bonds, may be ascribed to the hydrogen bonding.

The hydrogen bonding system comprises one infinite O–H···O chain, running along a fourfold screw axis, one four-membered, finite O–H···O chain around a fourfold inversion center, and two isolated C–H···O bonds. The two O–H···O bonds are both of intermediate strength. O(1) participates in planar (trigonal) fashion in the infinite chain, whereas O(3) participates in a more pyramidal (tetrahedral) way in the four-membered chain. The difference in hybridization may influence the C–O bond lengths.

As could be expected the acidic C(2)-proton participates in a hydrogen bond [to O(5)]. The strength of this interaction is difficult to judge, but using normalized C–H bond lengths (Table 6) the H···O distance becomes about 0.5 Å shorter than the van der Waals' distance. Among the 59 short (C–)H···O contacts listed by Taylor and Kennard[4] only 5 are shorter, indicating that this is a comparatively strong interaction.

More surprising is the short (C(3)–)H···O(5) distance, which is only slightly longer than that of the C(2)-proton. This contact may be the result of the packing arrangement, but it seems quite clear that it is an attractive interaction. The geometry is as required for a hydrogen bond, and the forementioned shortening of the C(3)–C(2) bond as compared to C(1)–C(2) is just what one may expect as a result of such an interaction.

The planar parts of two centrosymmetrically related molecules have a partial overlap of about 40 % and are separated by 3.56 Å.

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