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The Crystal Structures of Two Modifications of 3,5-Dinitro-L-tyrosine

By VIVIAN CODY,* DAVID A. LANGS AND JOHN P. HAZEL

Medical Foundation of Buffalo, Inc., 73 High Street, Buffalo, New York 14203, USA

Abstract

The crystal and molecular structure of 3,5-dinitro-L-tyrosine (DNT) has been determined in two crystalline modifications. Crystal (I), diaquasodium 3,5-dinitro-L-tyrosinate monohydrate [$C_9H_8N_3O_7^-.(H_2O)_2^-$ $Na^+.H_2O$] has a triclinic lattice, $P1$, $Z = 2$, $a = 8.271$ (3), $b = 13.357$ (5), $c = 6.864$ (2) Å, $\alpha = 110.4$ (3), $\beta = 97.0$ (2), and $\gamma = 92.7$ (3)°; crystal (II), 3,5-dinitro-L-tyrosine monohydrate ($C_9H_9N_3O_7.H_2O$), has an orthorhombic lattice, $P2_12_12_1$, $Z = 4$, $a = 7.8877$ (3), $b = 20.1926$ (6) and $c = 7.4242$ (3) Å. The two dinitro-L-tyrosine molecules in crystal (I) differ

primarily in their amino acid conformations; one [(IB)] has the carbonyl group extended, while in the other [(IA)] it is folded back over the ring. The conformation in crystal (II) has the carbonyl group extended, similar to that of one of the forms observed in crystal (I). The nitrate groups are nearly coplanar with their respective rings in crystal (I), while they deviate more significantly from coplanarity in crystal (II). The phenolic bonds in the two DNT molecules in crystal (I) are significantly different from each other (1·298/1·234 Å); that in molecule (IA) is a hydroxyl with an intramolecular hydrogen bond and that in (IB) is a phenoxide ion. The phenolic bond in crystal (II) (1·306 Å) has the same geometry as that in (IA) but has no intramolecular hydrogen bond. The sodium ions in

* To whom correspondence should be addressed.

crystal (I) form two distorted octahedra which share a common edge. They fill their coordination sphere using four water molecules and the carbonyl and nitro oxygens from the two dinitrotyrosine molecules. The remaining waters are hydrogen bonded to other waters in the cell.

1. Introduction

Dinitrotyrosine (DNT) has been shown, both *in vivo* and *in vitro*, to inhibit effectively the deiodination of iodotyrosines in the thyroid gland (Green, 1968; Greer & Grimm, 1968; Haibach, 1971), without any other important effect on thyroid function. Thus, DNT treatment affords a model for the human dehalogenase defect. By provoking iodotyrosine secretion and subsequent loss of iodine, DNT can exaggerate the effects of a low iodine intake, producing goitrous hypothyroidism despite a rapid rate of iodine turnover in the thyroid.

The structure determination of 3,5-dinitrotyrosine (Fig. 1) was undertaken to compare its conformational features with those of the thyroid hormone precursors, mono- and diiodotyrosine.

DNT crystallized in two modifications: as a sodium hydrate salt and as a simple monohydrate. Both crystal structures are described here.

Table 1. *Crystal data for 3,5-dinitro-L-tyrosine*

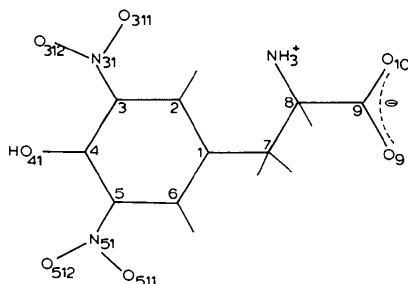|	(I)	(II)
Formula	$C_9H_8N_3O_7^-.(H_2O)_2Na^+.H_2O$	$C_9H_9N_3O_7.H_2O$
M_r	348·23	289·20
Space group	$P\bar{1}$	$P2_12_12_1$
a (Å)	8·271 (3)	7·8877 (3)
b (Å)	13·357 (5)	20·1926 (6)
c (Å)	6·864 (2)	7·4242 (3)
α (°)	110·4 (3)	
β (°)	97·0 (2)	
γ (°)	92·7 (3)	
Z	2	4
V (Å³)	702	1182
D_c (Mg m⁻³)	1·65	1·62
λ (Å)	1·5418	1·5418
R	0·065 (2190 observed data)	0·052 (1316 observed data)
	0·070 (2369 total data)	0·057 (1427 total data)

Fig. 1. Numbering scheme used for 3,5-dinitro-L-tyrosine.

2. Experimental

Crystal (I)

Bright-red crystals were grown at room temperature from a sodium hydroxide solution of 3,5-dinitro-L-tyrosine (Sigma Chemical Company). Preliminary diffraction analysis showed the crystals to be triclinic with two molecules in the asymmetric unit.

The cell dimensions were determined from a least-squares refinement of accurately measured values of 2θ for 46 high-angle reflections. The crystal data are listed in Table 1. A rectangular crystal 0·14 × 0·16 × 0·24 mm with well defined faces was selected for data collection and mounted with the a^* axis parallel to the ψ axis of a General Electric XRD-5 diffractometer. The intensities of all reflections (2368) with $2\theta < 130°$ were measured by the stationary crystal–stationary counter method with Cu $K\alpha$ ($\lambda = 1·5418$ Å) radiation monochromatized by balanced Ni and Co filters. 2190 reflections were considered observed, having intensities greater than twice their estimated standard deviations. No significant changes were observed in the intensities of the standard reflections measured during data collection. The shape anisotropy of the crystal measured at $\chi = 90°$ indicated a less than 5% variation in intensity over the θ range of data collection. The intensities were also corrected for Lorentz and polarization effects.

The structure was solved by direct methods using *QTAN* (Langs & DeTitta, 1977). All nonhydrogen atoms were located in the resulting E map. All H atoms of DNT were located from three-dimensional difference Fourier maps, but not all H positions of the water molecules were located. The H positions were not refined and isotropic B values were set at 3·0 Å² for all H. Refinement was terminated when there was no further improvement in the e.s.d.'s. The structure was refined by full-matrix least squares using all data to a final R index ($R = \sum \|F_o| - |F_c\|/\sum |F_o|$) of 0·070. A Hughes (1941) weighting scheme was used with $w = F_o/8·0$ if $F_o < 8·0$; $w = 8·0/F_o$ if $F_o \geq 8·0$. The function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$.

Crystal (II)

Orange-red crystals were grown at room temperature from ethanol solutions of 3,5-dinitro-L-tyrosine (Sigma Chemical Company). Preliminary diffraction analysis showed the crystals to be orthorhombic with one molecule in the asymmetric unit.

The cell dimensions were determined from a least-squares refinement of 37 hkl reflections having $2\theta > 80°$ with Cu $K\alpha$ radiation. The crystal data are also listed in Table 1. A well shaped crystal 0·12 × 0·20 × 0·16 mm was selected for intensity-data collection. All

Table 2. *Positional parameters and their e.s.d.'s for crystals* (I) *and* (II)

Crystal (I)	x	y	z
Na₁	0·3044	0·0071	0·5676 (0)
Na₂	0·2642 (3)	0·7993 (2)	0·7903 (4)
O(1W)	0·9788 (6)	0·7791 (3)	0·6743 (7)
O(2W)	0·3259 (6)	0·8203 (3)	0·4569 (6)
O(3W)	0·5035 (7)	0·8479 (5)	0·0565 (8)
O(4W)	0·0080 (5)	0·9748 (3)	0·4666 (7)
O(5W)	0·5968 (7)	0·7125 (4)	0·3340 (9)
O(6W)	0·7581 (9)	0·9179 (7)	0·8691 (14)
C(1)	0·2769 (6)	0·2834 (4)	0·1643 (8)
C(2)	0·2440 (7)	0·3858 (4)	0·2716 (8)
C(3)	0·3695 (7)	0·4666 (4)	0·3837 (8)
C(4)	0·5364 (7)	0·4504 (4)	0·3851 (7)
C(5)	0·5654 (6)	0·3412 (4)	0·2878 (7)
C(6)	0·4388 (7)	0·2618 (4)	0·1797 (8)
C(7)	0·1384 (7)	0·2013 (4)	0·0297 (7)
C(8)	0·1056 (6)	0·1050 (4)	0·0978 (7)
C(9)	0·2362 (7)	0·0280 (4)	0·0688 (8)
N(8)	0·0699 (6)	0·1410 (4)	0·3186 (7)
N(31)	0·3147 (6)	0·5689 (4)	0·4946 (8)
N(51)	0·7270 (6)	0·3086 (4)	0·2924 (7)
O(9)	0·2785 (7)	−0·0053 (4)	−0·1106 (6)
O(10)	0·2944 (6)	0·0015 (4)	0·2196 (6)
O(41)	0·6526 (5)	0·5283 (3)	0·4614 (6)
O(311)	0·1748 (6)	0·5866 (4)	0·4577 (10)
O(312)	0·4120 (7)	0·6339 (4)	0·6369 (8)
O(511)	0·7465 (6)	0·2136 (4)	0·1996 (10)
O(512)	0·8455 (6)	0·3718 (5)	0·3834 (9)
C(1*)	0·7097 (7)	0·4408 (4)	0·9127 (8)
C(2*)	0·5453 (7)	0·4607 (4)	0·8979 (8)
C(3*)	0·4247 (7)	0·3782 (4)	0·8008 (8)
C(4*)	0·4519 (7)	0·2657 (4)	0·7128 (7)
C(5*)	0·6248 (7)	0·2541 (4)	0·7387 (8)
C(6*)	0·7464 (7)	0·3378 (4)	0·8288 (8)
C(7*)	0·8418 (7)	0·5319 (4)	1·0335 (9)
C(8*)	0·8584 (7)	0·6200 (4)	0·9420 (8)
C(9*)	0·9704 (7)	0·7156 (4)	1·1023 (8)
N(8*)	0·9287 (6)	0·5826 (4)	0·7454 (7)
N(31*)	0·2578 (6)	0·4074 (3)	0·7913 (6)
N(51*)	0·6825 (6)	0·1498 (4)	0·6734 (8)
O(9*)	0·9065 (6)	0·7658 (3)	1·2567 (6)
O(10*)	1·1118 (6)	0·7346 (4)	1·0657 (7)
O(41*)	0·3429 (5)	0·1908 (3)	0·6288 (6)
O(311*)	0·2365 (6)	0·5015 (4)	0·8772 (10)
O(312*)	0·1422 (6)	0·3421 (4)	0·6976 (9)
O(511*)	0·8258 (6)	0·1414 (4)	0·6527 (10)
O(512*)	0·5880 (6)	0·0705 (4)	0·6522 (11)

Table 2 (*cont.*)

Crystal (II)	x	y	z
C(1)	0·5090 (3)	0·68507 (10)	0·6765 (3)
C(2)	0·4142 (3)	0·74235 (11)	0·7034 (3)
C(3)	0·4920 (3)	0·80024 (11)	0·7541 (3)
C(4)	0·6688 (3)	0·80730 (10)	0·7791 (3)
C(5)	0·7602 (3)	0·74728 (10)	0·7514 (3)
C(6)	0·6812 (3)	0·68821 (10)	0·7011 (3)
C(7)	0·4235 (3)	0·61972 (11)	0·6312 (3)
C(8)	0·3513 (3)	0·58582 (9)	0·8003 (3)
C(9)	0·2795 (3)	0·51771 (10)	0·7468 (4)
N(8)	0·4848 (3)	0·57722 (10)	0·9394 (3)
N(31)	0·3806 (3)	0·85642 (10)	0·7934 (4)
N(51)	0·9414 (3)	0·74493 (10)	0·7753 (3)
O(9)	0·3830 (3)	0·47011 (8)	0·7588 (4)
O(10)	0·1325 (2)	0·51401 (9)	0·6971 (3)
O(41)	0·7443 (2)	0·86317 (8)	0·6170 (3)
O(311)	0·2789 (3)	0·87405 (12)	0·6801 (5)
O(312)	0·3891 (4)	0·88111 (13)	0·9432 (4)
O(511)	1·0194 (3)	0·69942 (10)	0·7005 (4)
O(512)	1·0141 (3)	0·78667 (10)	0·8687 (3)
O(W1)	0·7687 (3)	0·52413 (10)	0·7564 (5)

The structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971) and NQEST (DeTitta, Edmonds, Langs & Hauptman, 1975). All nonhydrogen atoms were located in the resulting E maps. All H atoms but one water H were located from three-dimensional difference Fourier maps. Both the positional and isotropic thermal parameters for the H atoms were refined. Refinement was terminated when there was no further improvement in the e.s.d.'s. The structure was refined by full-matrix least squares using all data to a final R index of 0·057. The weights used in the final refinement were the quantities $(1/\sigma_F^2)$ where σ_F is defined by Stout & Jensen (1968; equation H.14) and the instability correction was 0·06. This value increases σ_F for reflections with a large $|F|$ and prevents them from controlling the refinement.

The least-squares programs are part of the Enraf–Nonius crystallographic package for the PDP 11/45 computer. All scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

The final fractional coordinates for both crystals (I) and (II) are listed in Table 2.* Fig. 1 shows the numbering scheme for dinitrotyrosine.

3. Results and discussion

The bond lengths and angles calculated from the fractional coordinates in Table 2 are given in Fig. 2.

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* Lists of structure factors and anisotropic thermal parameters for both (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34385 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

X-ray measurements were made on an Enraf–Nonius CAD-4 automated diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å).

The intensities of 1427 (1316 observed) independent reflections with $\theta < 75°$ were measured on the diffractometer with a 2θ–θ sweep of 1·2° + 0·15 (tan θ). No significant changes were observed in the intensities of the standard reflections measured during data collection. A reflection was considered unobserved if the net count was less than twice the standard deviation of the background. Intensities were corrected for Lorentz and polarization factors; however, no absorption correction was made.
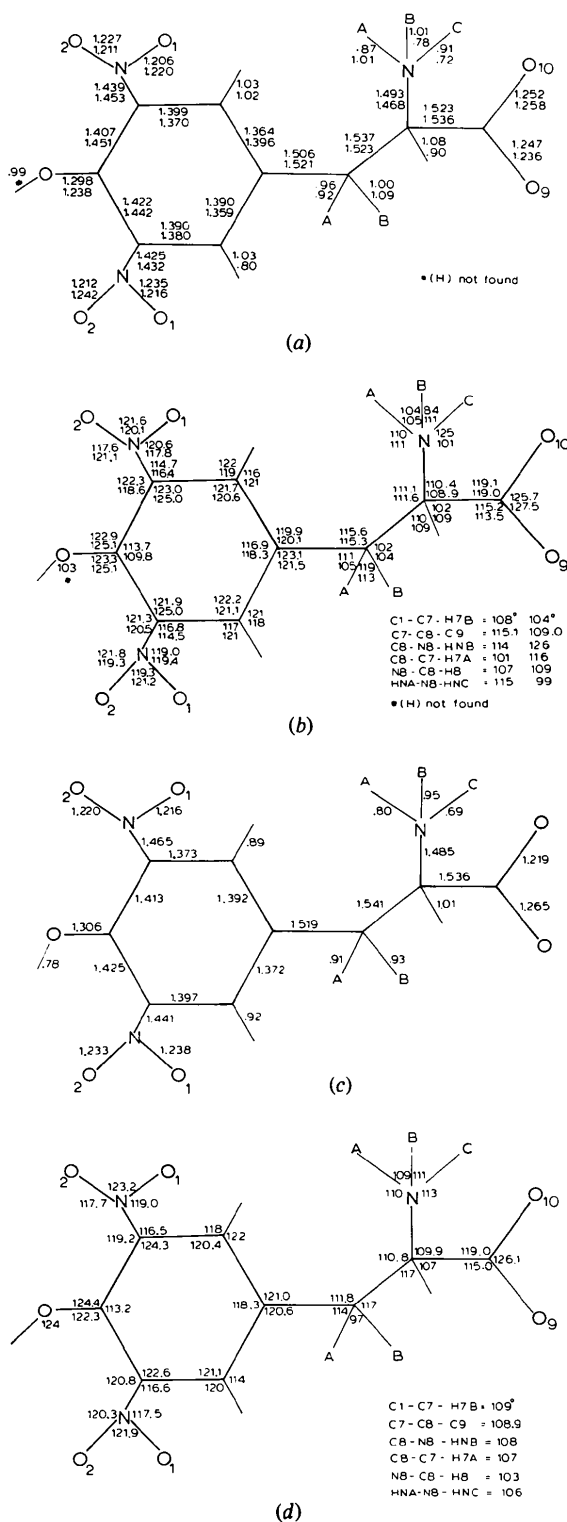
Fig. 2. (a) Bond lengths (Å) for molecules (IA) and (IB) of diaquasodium 3,5-dinitro-L-tyrosinate monohydrate; (b) bond angles (°) of molecules (IA) and (IB); the upper numbers refer to molecule (IA) in each case. (c) Bond lengths (Å) for molecule (II), 3,5-dinitro-L-tyrosine monohydrate; (d) bond angles (°) for molecule (II).

The estimated standard deviations of the bond lengths and angles for the nonhydrogen atoms in crystal (I) are 0·007 Å and 0·4° and in crystal (II) they are 0·003 Å and 0·2° respectively. The e.s.d.'s involving the hydrogens of crystal (II) are 0·03 Å and 1·4°. The amino acid side chains in all three DNT molecules are in the zwitterion form.

The major conformational differences among the three DNT molecules are listed in Table 3 and are illustrated in Fig. 3. The two molecules in crystal (I) differ primarily in their amino acid conformations; molecule (IA) has the carbonyl group folded over the ring (χ^1 = 57°) and (IB) has the carbonyl group extended (χ^1 = −71°). DNT in crystal (II) is also in the extended carbonyl conformation. The type of conformer observed in crystal (I) has also been reported in structures which have two amino acids coordinated to the same metal ion (van der Helm & Tatsch, 1972). The rotational parameters for these DNT molecules fall within the ranges (Table 3) observed in many aromatic amino acids (Cody, Duax & Hauptman, 1973).

The conformation of DNT in crystal (II) is almost identical to that observed in molecule (A) of diiodotyrosine ethyl ester (Cody, Duax & Norton, 1971) while that of molecule (IB) is similar to the other conformer of diiodotyrosine ethyl ester.

The sodium ions in crystal (I) form two distorted octahedra (Fig. 4) which share a common edge. They fill their coordination sphere using four waters and the carboxyl and nitro O atoms from the two dinitrotyrosine molecules. This type of shared octahedra has also been reported in other sodium complexes (Rao & Mallikarjunan, 1975; Verbist, Putzeys, Piret & Van Meerssche, 1971; Mandel & Mandel, 1976). While the Na—O distances shown in Table 4 agree with those observed in other octahedral Na structures, there is one exceptionally long (2·74 Å) Na—O distance to a carboxyl O of molecule (IB). The octahedral coordination angles also deviate significantly from their ideal values.

The ring geometry of the three DNT molecules (Fig. 2, Table 5) suggests two molecular species are present.

Table 3. Amino acid conformational comparison

	χ^{1*}	χ^2	ψ	Reference
3,5-Dinitro-L-tyrosine				This study
(IA)	57°	67°	3°	
(IB)	−71	120	−13	
(II)	−55	96	−30	
3,5-Diiodo-L-tyrosine ethyl ester				
(A)	−56	95	−32	Cody et al. (1971)
(B)	−72	99	−19	
3,5-Diiodo-L-tyrosine.H₂O	180	90	−58	Hamilton & Steinrauf (1967)
3-Iodotyrosine	177	81	66	V. Cody (unpublished)

* χ^1 = C(1)−C(7)−C(8)−N(8); χ^2 = C(2)−C(1)−C(7)−C(8); ψ = N(8)−C(8)−C(9)−O(10).

Table 4. *Sodium coordination in crystal* (I)

Asterisks refer to the atom names of molecule (1B).

|							
Na₁—O(9)	2·307 Å	O(9)—Na₁—O(2W)	85·0°	O(2W)—Na₁—O(512*)	99·6 Å	O(512*)—Na₁—O(10)	92·3°
O(2W)	2·363	O(512*)	96·0	O(10)	90·8	O(41*)	68·8
O(10)	2·355	O(10)	171·3	O(41*)	164·7	O(4W)	168·7
O(41*)	2·340	O(41*)	105·7	O(4W)	90·5	O(10)—Na₁—O(41*)	80·1
O(4W)	2·441	O(4W)	90·3	O(41*)—Na₁—O(4W)	100·4	O(4W)	82·2
O(512*)	2·386						
Na₂—O(9)	2·450	O(9)—Na₂—O(2W)	79·0	O(2W)—Na₂—O(1W)	91·7	O(1W)—Na₂—O(10*)	72·6
O(2W)	2·510	O(1W)	92·4	O(10*)	161·3	O(312)	115·5
O(312)	2·536	O(10*)	110·9	O(312)	79·2	O(3W)	153·8
O(10*)	2·744	O(312)	144·9	O(3W)	111·9	O(10*)—Na₂—O(312)	98·4
O(1W)	2·368	O(3W)	81·1	O(3W)—Na₂—O(312)	82·0	O(3W)	86·0
O(3W)	2·419						
Na₁—Na₂	3·626						
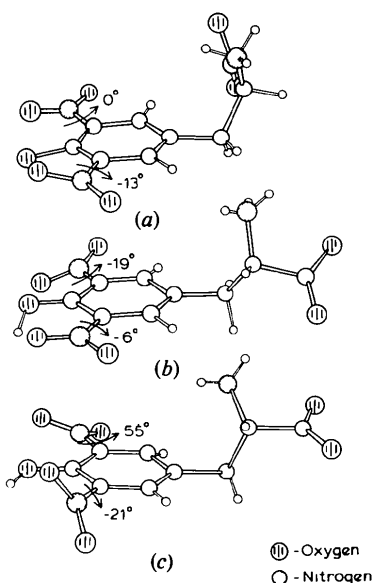
Fig. 3. 3,5-Dinitro-L-tyrosine: molecular conformations for crystals (a) (1A), (b) (1B) and (c) (II); nitrate torsion angles are also shown.

Fig. 4. Sodium coordination sphere in crystal (1).

In molecules (1A) and (II), the C—O distance and the observation of the —OH hydrogen atom indicate the presence of a hydroxyl function, whereas in molecule (1B) the absence of the H and the shorter C—O distance are consistent with phenoxide ion formation.

The average amino nitrogen C—N distances based on the results of a number of aromatic amino acid structures (Cody, Duax & Hauptman, 1973) are: —NH₃⁺ (1·495 Å), —NH₂ (1·478 Å) and —NHCO— (1·450 Å). In molecules (1A) and (II), the amino N bond lengths (Fig. 2) and hydrogen-bonding arrangements are consistent with normal zwitterion formation. The C—N distance in molecule (1B) is somewhat shorter, more in line with an —NH₂ species.

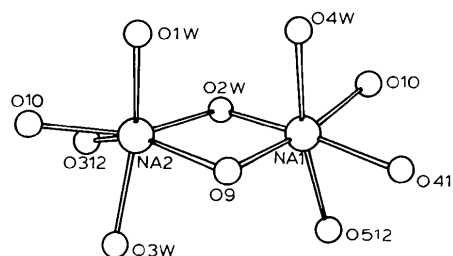The distribution of charges in crystal (I) is not clearly delineated. One of the sodium ion charges is balanced by the phenoxide ion of molecule (1B). Molecule (1A), on the other hand, appears to be a neutral species. If the shorter C—N distance in molecule (1B) is significant, then not all three H atoms are correctly positioned. However, there is no indication from the Fourier maps that any of these positions are less well resolved than any of the other H positions in the structure. If this is, in fact, an —NH₂ group, molecule (1B) would bear two formal negative charges, satisfying both sodium charges. The coordination sphere of Na₂ is also less tightly held than that of Na₁, as indicated by the Na—O distances in Table 4. However, a more likely situation is that the second negative charge is diffused over the structure.

3,5-Dinitro-L-tyrosine resembles picric acid in that it has a 2,6-dinitrophenol ring system. The average geometries of a charged picrate salt and a neutral picric acid species are listed in Table 5 along with the related parameters from these structures. Molecule (1B) has the picrate ion geometry while molecules (1A) and (II) closely resemble the neutral picric acid species. Thus the effects of di-*ortho* substitution on the ring geometry are observed in this system as well.

It is well established that nitro groups tend to lie near the aromatic plane unless prevented by steric effects. Also, the ring angle to which the nitro group is attached is always larger than 120°. These effects are generally attributed to resonance interactions between the nitro

group and the ring. In a comprehensive analysis of factors affecting aromatic nitro-group conformation, Holden & Dickinson (1977) showed that at 'equilibrium' the O—N—O angle of an aromatic nitro group is 126·4°, the two C—N—O angles are equal, and the two C—C—N angles are equal. With the exception of the O—N—O geometry, these characteristics are generally maintained in these three DNT molecules (Fig. 2). The 55° twist of the N(51) nitro group in crystal (II) is somewhat large. The two nitro O atoms of this group are both 3·08 Å from the water molecule. Perhaps·this interaction is stronger than the tendency toward coplanarity with the ring.

As shown in Table 6, both crystals have an extended network of intermolecular hydrogen bonds. In addition to the sodium coordination and intermolecular hydrogen bonding with DNT and water in crystal (I), there is also an intramolecular hydrogen bond. It has been shown that nitro compounds can participate in both intermolecular and intramolecular hydrogen bonding (Baitinger, von Schleyer, Murty & Robinson, 1964). In particular, p-nitrophenol groups, because of resonance,
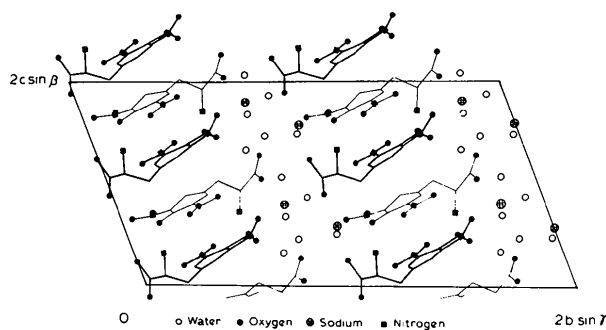

(a)

(b)

Fig. 5. (a) Packing diagram for diaquasodium 3,5-dinitro-L-tyrosinate monohydrate. The large circles are Na, filled circles O and squares N. The dark molecules are above the light ones. (b) Packing diagram for 3,5-dinitro-L-tyrosine monohydrate. The filled circles are O, squares N.

can increase the proton donor ability of the OH group and the proton acceptor ability of the NO_2, forming a strong intramolecular hydrogen bond. Such is the case with molecule (I*A*) (Table 6). The O(41) H atom makes an angle of 144° with O(512) of the coplanar nitro group. This type of intramolecular hydrogen bond was also observed in picric acid structures (Herbstein & Kaftory, 1976; Jensen, 1975; Soriano-Garcia, Srikrishnan & Parthasarathy, 1978). The geometry of molecule (I*A*) is consistent with the intramolecular hydrogen-bonded resonance structure proposed by Baitinger et al. (1964). Although the ring geometry in crystal (II) is similar to that of (I*A*), no intramolecular hydrogen bond is formed. Instead the O(41) H atom participates in an intermolecular hydrogen bond with O(9).

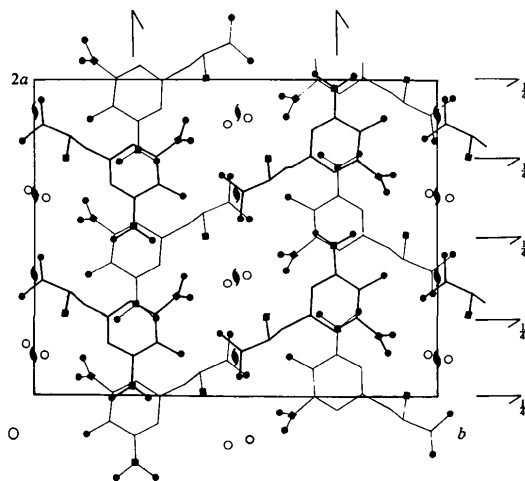Table 5. *Comparison of the 3,5-dinitrophenoxy moiety with picrates*

	Average picrate salt*	(I*B*)	Average picric acid†	(I*A*)	(II)
C(4)–O(41)	1·244 Å	1·234 Å	1·323 Å	1·298 Å	1·306 Å
C(3)–C(4)	1·457	1·451	1·405	1·407	1·413
C(4)–C(5)	1·446	1·442	1·404	1·422	1·425
C(3)–C(4)–C(5)	111·6°	109·8°	115·4°	113·7°	113·2°
C(2)–C(3)–C(4)	124·2	125·0	123·5	123·0	124·3
C(4)–C(5)–C(6)	124·1	125·0	122·6	121·9	122·6
O(311)–N(31)–O(312)		120·1		121·6	123·2
O(511)–N(51)–O(512)		121·1		119·3	121·9

* These averages are taken from the following structure determinations: Gerdil (1972); J. F. Griffin and P. Coppens (unpublished); Maartmann-Moe (1969); Thewalt & Bugg (1972).

† These averages are taken from the following structure determinations: Jensen (1975); Herbstein & Kaftory (1976); Soriano-Garcia et al. (1978).

Table 6. *Hydrogen bonding in* (I) *and* (II)

X–H⋯Y	X–H	H⋯Y	X⋯Y	∠X–H⋯Y
Crystal (I)				
N(8)–H(8*A*)⋯O(41*)	0·87 Å	1·94 Å	2·79 Å	163°
—H(8*B*)⋯O(4*W*)	1·01	1·82	2·80	162
—H(8*C*)⋯O(511)	0·91	2·29	3·00	134
N(8*)–H(8*A*)⋯O(1*W*)	1·01	1·87	2·85	163
—H(8*B*)⋯O(311*)	0·78	2·29	2·97	146
·H(8*C*)⋯O(41)	0·72	2·02	2·71	159
O(1*W*)–H(1*A*)⋯O(6*W*)	1·04	1·74	2·78	177
—H(1*B*)⋯O(9*)	1·03	1·99	2·80	134
O(2*W*)– ⋯O(5*W*)			2·78	
— ⋯O(10*)			2·86	
O(3*W*)– ⋯O(9), O(10)			3·17	
			2·77	
—H(3*B*)⋯O(5*W*)	1·12	2·04	3·11	158
O(4*W*)–H(4*A*)⋯O(9*)	1·05	1·69	2·69	159
—H(4*B*)⋯O(511*)	0·85	2·04	2·77	143
O(5*W*)–H(5*A*)⋯O(2*W*)	1·15	1·64	2·78	173
—H(5*B*)⋯O(41)	1·02	1·91	2·92	170
O(6*W*)–⋯O(3*W*)			2·88	
—H(6*B*)⋯O(512*)	1·06	2·35	3·20	136
O(41)–H(41)⋯O(512)	0·99	1·77	2·64	144
Crystal (II)				
N(8)–H(9*A*)⋯O(312)	0·78	2·35	3·10	164
—H(8*B*)⋯O(10)	0·95	1·87	2·81	170
—H(8*C*)⋯O(*W*1)	0·69	2·15	2·83	170
O(41)–H(41)⋯O(9)	0·78	1·67	2·45	171
O(*W*1)– ⋯N(8)			2·83	
— ⋯O(10)			2·91	

As can be seen from Table 6 and Fig. 5(a), crystal (I) has an extended three-dimensional network of inter-molecular hydrogen bonds involving the waters of hydration. The Na ions and their waters of hydration form layers between columns of DNT. The two DNT molecules themselves are stacked over one another with C(6)–C(4*) (3·24 Å) being the closest contact. The two molecules are rotated with respect to each other in such a way that the nitro groups do not lie directly over the ring. The DNT form alternating layers with a head-to-head or tail-to-tail arrangement.

In crystal (II) (Fig. 5b), the DNT molecules also form the same alternating pattern; however, they are more compact. The DNT are also oriented in such a way that the nitro groups lie over the ring. The closest contacts between the layers are within the normal charge-transfer distances with C(2)–O(511) 3·23 Å, C(3)–O(512) 3·31 Å and C(6)–O(311) 3·19 Å. The nitro group at C(5) may be rotated so far from coplanarity to facilitate these close contacts.

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Structure of cis-3-(4-Bromophenyl)-4a,7a-dihydro-6,7a-dimethyl-4a,5-diphenyl-7H-cyclopenta-1,4,2-dioxazine, the Product of a Regio- and Stereospecific Isomerization

By CHUNG CHIEH AND DONALD MACKAY

Guelph–Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Abstract

The adduct of 1,4-dimethyl-2,3-diphenylcyclopenta-diene and p-bromonitrosocarbonylbenzene underwent a regio- and stereospecific isomerization leading to the title compound, $C_{26}H_{22}BrNO_2$. The colorless crystals grown from ethanol (with a trace of benzene) are monoclinic with $a = 13·949$ (4), $b = 10·588$ (2), $c = 16·753$ (3) Å, $\beta = 119·1$ (1)°, space group $P2_1/c$ and $Z = 4$. The structure was determined from 2105 observed reflections measured by the θ–2θ scan technique using graphite-monochromated Mo $K\alpha$ radiation