C21—N21	1.147 (6)	C12—C13	1.510 (7)
C3—C4	1.493 (8)	C13—C14	1.520 (7)
C4—C5	1.528 (8)	C14—C15	1.504 (7)
C5—C6	1.517 (6)	C15—N16	1.509 (5)
C6—C7	1.527 (7)	N16—C17	1.508 (5)
C7—C17	1.518 (6)		
C10—N1—C6	112.2 (3)	C8—C7—C6	110.2 (4)
C10—N1—C2	110.8 (3)	C9—C8—C7	106.2 (4)
C6—N1—C2	112.1 (3)	C10—C9—C8	109.2 (4)
N1—C2—C21	108.4 (4)	C10—C9—C11	113.2 (4)
N1—C2—C22	112.4 (4)	C8—C9—C11	112.1 (3)
C21—C2—C22	109.4 (4)	N1—C10—C9	112.3 (3)
N1—C2—C3	109.4 (4)	C12—C11—N16	111.0 (3)
C21—C2—C3	108.1 (4)	C12—C11—C9	113.9 (4)
C22—C2—C3	109.1 (4)	N16—C11—C9	109.3 (3)
N21—C21—C2	177.2 (5)	C13—C12—C11	112.6 (4)
C4—C3—C2	113.7 (4)	C12—C13—C14	110.2 (4)
C3—C4—C5	108.9 (4)	C15—C14—C13	111.1 (4)
C6—C5—C4	111.9 (4)	C14—C15—N16	111.3 (4)
N1—C6—C5	110.6 (4)	C17—N16—C15	112.5 (3)
N1—C6—C7	110.8 (3)	C17—N16—C11	112.8 (3)
C5—C6—C7	112.5 (4)	C15—N16—C11	112.4 (3)
C17—C7—C8	108.8 (4)	N16—C17—C7	111.8 (3)
C17—C7—C6	115.0 (4)		

H atoms were positioned riding on their parent C atoms, with fixed C—H distances and idealized angles, and with $U_{iso}(H) = 1.2U_{eq}(C)$. The minor disorder component of the anion was initially restrained to have a similar geometry to the major component and was subsequently held fixed as a rigid group.

Data collection: $P2_1$ software. Cell refinement: $P2_1$ software. Data reduction: *PRADIR* (Jaskólski, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *Stereochemical Workstation* (Siemens, 1989). Software used to prepare material for publication: *SHELXL*93.

This study was supported jointly by Projects No. 2 0759 91 01 KBN and S/II.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: CF1028). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Co-Crystallization of Stereoisomers of *N,N'*-Bis(2-phenyl-5-hydroxymethyl-1,3-dioxan-5-yl)ethanediamide

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(*Received 21 September 1995; accepted 20 October 1995*)

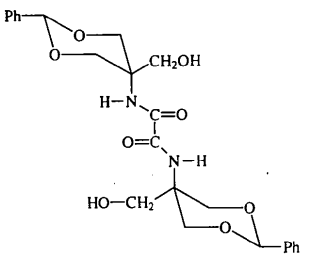
Abstract

X-ray analysis has revealed that two stereoisomers of the title compound, $C_{24}H_{28}N_2O_8$, co-crystallize in form (I). The unit cell of (I) contains equal numbers of the *N,N'*-bis(*trans*-2-phenyl-5-hydroxymethyl-1,3-dioxan-5-yl)ethanediamide, (I*a*), and the *N,N'*-bis(*cis*-2-phenyl-5-hydroxymethyl-1,3-dioxan-5-yl)ethanediamide, (I*b*), stereoisomers, each lying about crystallographic inversion centres. Fractional crystallization of the first mother liquor afforded crystals (II) containing only molecules of stereoisomer (I*a*), also with crystallographic inversion symmetry. The stereoisomer (I*a*) is Z-shaped in (I) and (II), whereas (I*b*) is maximally extended. In both (I) and (II), the molecules are linked about inversion centres by O—H···O hydrogen bonds.

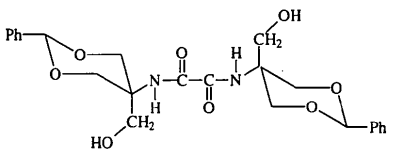
Comment

The co-crystallization of enantiomers, in a 1:1 ratio, is relatively commonplace as evidenced by the popularity of such space groups as $P2_1/c$. In contrast, from the lack of reports in the literature, co-crystallization of other types of stereoisomers is much rarer. We were able to prepare serendipitously (see *Experimental* section) crystals of (I) which we subsequently showed to contain equal numbers of two different stereoisomers, *N,N'*-bis(*trans*-2-phenyl-5-hydroxymethyl-1,3-dioxan-5-yl)ethanediamide, (I*a*) and *N,N'*-bis(*cis*-2-phenyl-5-hydroxymethyl-1,3-dioxan-

5-yl)ethanediamide, (I*b*). Fractional crystallization of the first mother liquor afforded pure crystals, (II), of the (I*a*) form of these stereoisomers. ^{1}H-NMR spectra showed that there is no interconversion of the isomers in solution.



(I*a*)



(I*b*)

In (I), both independent molecules [(I*a*) and (I*b*)] lie about inversion centres and the asymmetric unit contains two half molecules. The crystals of (II) contain only molecules of (I*a*), which also lie about inversion centres and the asymmetric unit in this case contains one half of a molecule.

Views of the two independent centrosymmetric molecules (I*a*) and (I*b*) in crystals of (I) are given in Figs. 1 and 2 respectively; molecule (I*a*) in crystals of (II) is shown in Fig. 3. In all three molecules [the two forms of (I*a*) and the one of (I*b*)], the 1,3-dioxan rings are in chair conformations with the phenyl substituents equatorial. The hydroxymethyl group attached to C5 of the dioxan ring is axial in both forms of (I*a*) and equatorial to the ring in (I*b*). As a result, the two isomers have quite distinct shapes: the *trans* isomer (I*a*) has a Z-shaped arrangement in both (I) and (II), while the *cis* isomer (I*b*) has a quasiplanar-type arrangement. Despite these differences, the two stereoisomers are clearly able to pack together in (I) in a regular manner. The main difference between molecule (I*a*) in (I) and in (II) is in the orientation of the terminal phenyl rings as shown by the torsion angles O1*A*—C2*A*—C7*A*—C12*A* 23.4 (3) in (I) and O1—C2—C7—C12 46.0 (6)° in (II). In (I*b*), the phenyl ring is rotated even more about the exocyclic C2*B*—C7*B* bond [O1*B*—C2*B*—C7*B*—C12*B* 99.8 (3)°]. Bond lengths (Table 2) are essentially as expected and, with the location of the relevant H atoms, establish the structures unequivocally.

In all the molecules there are inversion-symmetry-related pairs of intramolecular N—H···O hydrogen bonds (Table 3) between amide N—H groups and adjacent carbonyl O atoms. In both (I) and (II) the same type of intermolecular O—H···O hydrogen bonding between the hydroxymethyl hydroxyl group [O17*A* in (I), O17 in (II)] and carbonyl O atoms [O15*A* in (I), O15 in (II)] links (I*a*) molecules (Table 3). There is a further intermolecular hydrogen bond in (I) involving the hydroxymethyl group of molecule (I*b*) and a dioxan O atom of (I*a*) linking molecules about other inversion centres.

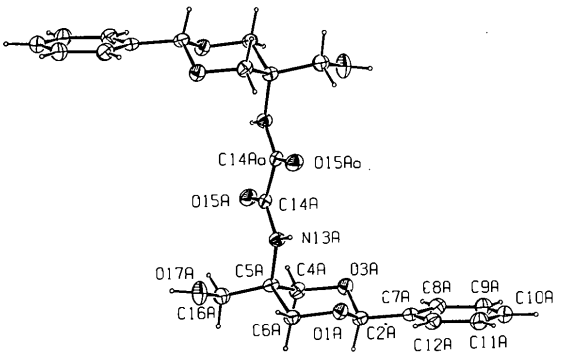


Fig. 1. A view of the bis-*trans* isomer (I*a*) in crystals of (I). Displacement ellipsoids are drawn at the 30% probability level. The atoms labelled with an 'a' are at symmetry position $2-x, 2-y, -z$.

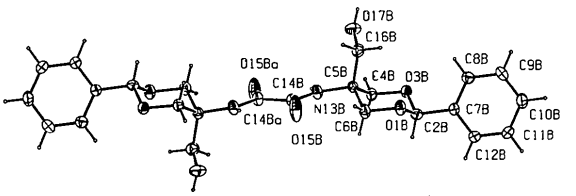


Fig. 2. A view of the bis-*cis* isomer (I*b*) in crystals of (I). Displacement ellipsoids are drawn as in Fig. 1. The atoms labelled with an 'a' are at symmetry position $1-x, 2-y, -z$.

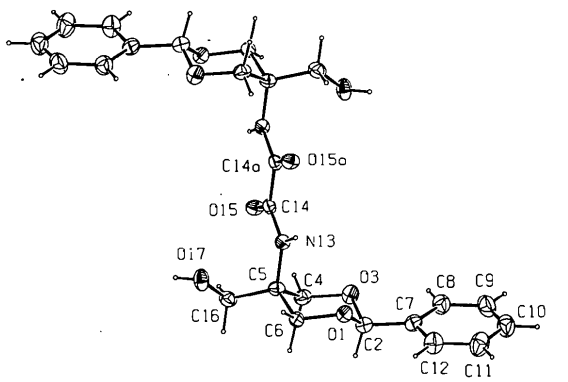


Fig. 3. A view of the bis-*trans* isomer (I*a*) in crystals of (II). Displacement ellipsoids are drawn as in Fig. 1. The atoms labelled with an 'a' are at symmetry position $1-x, -y, 2-z$.

Experimental

Three stereoisomers, (I*a*), (I*b*) and *N*-(*trans*-2-phenyl-5-hydroxymethyl-1,3-dioxan-5-yl)-*N'*-(*cis*-2-phenyl-5-hydroxymethyl-1,3-dioxan-5-yl)ethanediamide, (I*c*), were formed in a 1.3:1.8:1.0 ratio in the acid-catalyzed reaction of $(HOCH_2)_3CNHC(O)C(O)NHC(CH_2OH)_3$ with excess PhCHO. Crystal-

lization from aqueous acetone of the crude reaction product gave a first crop of crystals and recrystallization from Me_2CO/H_2O, gave crystals, (I), which we subsequently showed to contain a 1:1 mixture of the (I*a*) and (I*b*) stereoisomers. Repeated fractional crystallization, from EtOAc/Me_2CO, of the residue from the first mother liquor led to the separation of pure (I*a*) [compound (II)] and (I*c*) isomers; we were unable to prepare (I*c*) in a crystalline form for suitable for X-ray analysis.

Compound (I)

Crystal data

$C_{24}H_{28}N_2O_8$
M_r = 472.48
Monoclinic
$P2_1/c$
a = 10.3023 (9) Å
b = 6.6712 (7) Å
c = 33.0305 (4) Å
β = 95.489 (8)°
V = 2259.7 (3) Å^3
Z = 4
D_x = 1.389 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 10.0–12.0°
μ = 0.105 mm^{-1}
T = 294 (1) K
Plate
0.42 × 0.32 × 0.07 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3740 measured reflections
3537 independent reflections
2002 observed reflections [$I > 2\sigma(I)$]

R_{int} = 0.014
θ_{max} = 23.9°
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 37$
3 standard reflections
frequency: 120 min
intensity decay: no decay, variation 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0423
$wR(F^2)$ = 0.1075
S = 0.933
3537 reflections
309 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.007

$\Delta\rho_{max}$ = 0.288 e Å^{-3}
$\Delta\rho_{min}$ = −0.265 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Compound (II)

Crystal data

$C_{24}H_{28}N_2O_8$
M_r = 472.48
Monoclinic
$P2_1/c$
a = 6.2996 (11) Å
b = 31.2070 (12) Å
c = 6.378 (3) Å
β = 110.57 (2)°
V = 1173.9 (6) Å^3
Z = 2
D_x = 1.337 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 7.0–18.0°
μ = 0.101 mm^{-1}
T = 294 (1) K
Plate
0.42 × 0.32 × 0.07 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1414 measured reflections
1268 independent reflections
671 observed reflections [$I > 2\sigma(I)$]

R_{int} = 0.013
θ_{max} = 22.0°
$h = -6 \rightarrow 5$
$k = 0 \rightarrow 32$
$l = 0 \rightarrow 6$
3 standard reflections
frequency: 120 min
intensity decay: no decay, variation 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0517
$wR(F^2)$ = 0.1568
S = 0.909
1265 reflections
155 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0771P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 0.219 e Å^{-3}
$\Delta\rho_{min}$ = −0.231 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
(I)				
O1*A*	0.8476 (2)	0.9715 (3)	0.12113 (5)	0.0360 (4)
C2*A*	0.9652 (2)	0.9723 (4)	0.14655 (7)	0.0345 (6)
O3*A*	1.0734 (2)	0.9485 (3)	0.12368 (5)	0.0374 (5)
C4*A*	1.0690 (2)	0.7602 (4)	0.10258 (7)	0.0372 (7)
C5*A*	0.9421 (2)	0.7399 (4)	0.07522 (7)	0.0318 (6)
C6*A*	0.8301 (2)	0.7830 (4)	0.10050 (7)	0.0357 (6)
C7*A*	0.9790 (3)	1.1662 (4)	0.16993 (7)	0.0364 (7)
C8*A*	1.1010 (3)	1.2244 (5)	0.18718 (8)	0.0472 (7)
C9*A*	1.1142 (4)	1.3922 (5)	0.21163 (9)	0.0592 (9)
C10*A*	1.0068 (4)	1.5050 (5)	0.21886 (9)	0.0623 (10)
C11*A*	0.8859 (4)	1.4492 (5)	0.20128 (9)	0.0578 (9)
C12*A*	0.8714 (3)	1.2803 (4)	0.17691 (8)	0.0463 (7)
N13*A*	0.9358 (2)	0.8918 (3)	0.04281 (6)	0.0338 (5)
C14*A*	1.0180 (3)	0.9126 (4)	0.01465 (7)	0.0331 (6)
O15*A*	1.1158 (2)	0.8097 (3)	0.01130 (5)	0.0437 (5)
C16*A*	0.9290 (3)	0.5296 (4)	0.05754 (8)	0.0398 (7)
O17*A*	0.8075 (2)	0.5130 (3)	0.03392 (6)	0.0548 (6)
O1*B*	0.5398 (2)	1.4309 (3)	0.12943 (5)	0.0431 (5)
C2*B*	0.4942 (2)	1.6245 (4)	0.11869 (8)	0.0361 (6)
O3*B*	0.3710 (2)	1.6150 (3)	0.09568 (5)	0.0354 (4)
C4*B*	0.3783 (3)	1.5050 (4)	0.05905 (7)	0.0357 (6)
C5*B*	0.4238 (2)	1.2921 (4)	0.06871 (7)	0.0322 (6)
C6*B*	0.5560 (3)	1.3082 (4)	0.09443 (8)	0.0445 (7)
C7*B*	0.4772 (2)	1.7405 (4)	0.15699 (7)	0.0330 (6)
C8*B*	0.3669 (3)	1.7187 (4)	0.17709 (8)	0.0427 (7)
C9*B*	0.3504 (3)	1.8298 (4)	0.21130 (8)	0.0463 (7)
C10*B*	0.4450 (3)	1.9635 (5)	0.22587 (8)	0.0524 (8)
C11*B*	0.5555 (3)	1.9853 (5)	0.20612 (9)	0.0573 (9)
C12*B*	0.5717 (3)	1.8752 (4)	0.17186 (8)	0.0462 (7)
N13*B*	0.4356 (2)	1.1929 (3)	0.02938 (6)	0.0405 (6)
C14*B*	0.5134 (3)	1.0439 (4)	0.02139 (8)	0.0380 (7)
O15*B*	0.5981 (3)	0.9726 (4)	0.04477 (6)	0.0901 (9)
C16*B*	0.3268 (3)	1.1794 (4)	0.09210 (8)	0.0457 (7)
O17*B*	0.2004 (2)	1.2038 (3)	0.07151 (6)	0.0594 (6)
(II)				
O1	1.0502 (5)	0.10141 (10)	1.2065 (5)	0.0390 (9)
C2	0.9193 (10)	0.1394 (2)	1.1438 (8)	0.0441 (15)
O3	0.6889 (6)	0.12940 (10)	1.0305 (6)	0.0476 (10)
C4	0.6594 (9)	0.1069 (2)	0.8278 (8)	0.0428 (15)
C5	0.8017 (9)	0.0660 (2)	0.8680 (8)	0.0370 (14)
C6	1.0452 (8)	0.0784 (2)	1.0110 (8)	0.0399 (14)

C7	0.9436 (11)	0.1649 (2)	1.3496 (8)	0.0428 (15)
C8	0.7625 (11)	0.1856 (2)	1.3817 (10)	0.056 (2)
C9	0.7959 (14)	0.2110 (2)	1.5659 (12)	0.070 (2)
C10	1.0076 (16)	0.2163 (2)	1.7230 (11)	0.071 (2)
C11	1.1904 (13)	0.1957 (2)	1.6953 (10)	0.072 (2)
C12	1.1561 (11)	0.1707 (2)	1.5070 (9)	0.060 (2)
N13	0.7230 (7)	0.03502 (12)	0.9956 (6)	0.0322 (11)
C14	0.5177 (10)	0.01726 (15)	0.9234 (8)	0.0338 (13)
O15	0.3618 (6)	0.02756 (11)	0.7499 (5)	0.0433 (10)
C16	0.7866 (9)	0.0477 (2)	0.6417 (8)	0.0445 (15)
O17	0.8635 (6)	0.00442 (12)	0.6683 (5)	0.0501 (11)

Table 2. *Selected bond lengths (Å)*

Crystal	(I)	(I)	(II)
Molecule	(I*a*)	(I*b*)	(I*a*)
	n = *A*	*n* = *B*	*n* = –
O1*n*—C2*n*	1.407 (3)	1.409 (3)	1.419 (6)
O1*n*—C6*n*	1.434 (3)	1.439 (3)	1.431 (5)
C2*n*—O3*n*	1.414 (3)	1.417 (3)	1.410 (6)
C2*n*—C7*n*	1.506 (3)	1.507 (3)	1.495 (6)
O3*n*—C4*n*	1.435 (3)	1.423 (3)	1.425 (5)
C4*n*—C5*n*	1.522 (3)	1.520 (3)	1.530 (6)
C5*n*—C6*n*	1.514 (3)	1.539 (3)	1.533 (6)
C5*n*—N13*n*	1.471 (3)	1.473 (3)	1.458 (6)
C5*n*—C16*n*	1.521 (4)	1.520 (3)	1.524 (6)
N13*n*—C14*n*	1.324 (3)	1.319 (3)	1.331 (6)
C14*n*—C14*n*^{i}	1.538 (5)	1.530 (5)	1.523 (9)
C14*n*—O15*n*	1.233 (3)	1.206 (3)	1.236 (5)
C16*n*—O17*n*	1.415 (3)	1.420 (3)	1.424 (5)

Equivalent positions: for (I*a*) in (I) (i) = $2-x, 2-y, -z$; for (I*b*) in (I) (i) = $1-x, 2-y, -z$; for (I*a*) in (II) (i) = $1-x, -y, 2-z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
(I)				
N13*A*—H13*A*···O15*A*^{i}	0.86	2.28	2.695 (3)	109
N13*B*—H13*B*···O15*B*^{ii}	0.86	2.28	2.679 (3)	108
O17*A*—H17*A*···O15*A*^{iii}	0.82	2.00	2.778 (3)	158
O17*B*—H17*B*···O3*A*^{iv}	0.82	2.06	2.831 (3)	157
(II)				
N13—H13···O17^{v}	0.86	2.23	2.995 (5)	149
O17—H17···O15^{vi}	0.82	1.93	2.731 (5)	166

Symmetry codes: (i) $2-x, 2-y, -z$; (ii) $1-x, 2-y, -z$; (iii) $2-x, 1-y, -z$; (iv) $x-1, y, z$; (v) $2-x, -y, 2-z$; (vi) $1-x, -y, 1-z$.

Data collection was terminated at a θ value of 22° for (I) and 24° for (II) because of the absence of observable data. The diagrams were prepared using *ORTEP*II (Johnson, 1976) as implemented in *PLATON* (Spek, 1995*a*). Examination of the structures with the *SOLV* option in *PLATON* showed that there were no solvent-accessible voids in the crystal lattices. For all three stereoisomers, H atoms were refined as riding [default in *SHELXL*93 (Sheldrick, 1993) C—H 0.93–0.98, N—H 0.86 and O—H 0.82 Å].

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius 1992); cell refinement: *SET*4 and *CELDIM* (*CAD*-4 Software); data reduction: *DATRD*2 (*NRCVAX*94; Gabe, Le Page, Charland, Lee & White, 1989); program(s) used to solve structures: *SOLVER* (*NRCVAX*94); program(s) used to refine structures: *NRCVAX*94; *SHELXL*93 (Sheldrick, 1993); molecular graphics: *NRCVAX*94; *PLATON* (Spek, 1995*a*); *PLUTON* (Spek 1995*b*); software used to prepare material for publication: *NRCVAX*94; *SHELXL*93 and *WordPerfect*.

GF thanks NSERC (Canada) for research grants.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1322). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 231–235

Molecular Co-Crystals of Carboxylic Acids. 23.† The 1:1 Adducts of 3-Amino-1*H*-1,2,4-triazole with 5-Nitrosalicylic Acid and 3,5-Dinitrosalicylic Acid

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(*Received 24 October 1994; accepted 26 July 1995*)

Abstract

The structures of the 1:1 molecular adducts of the herbicide 3-amino-1*H*-1,2,4-triazole (amitrole, 3-AT) with 5-nitrosalicylic acid (5-NSA), 3-amino-2*H*,4*H*$^{+}$-1,2,4-triazolium 5-nitrosalicylate, $C_2H_5N_4^+.C_7H_4NO_5^-$, (1), and 3,5-dinitrosalicylic acid (DNSA), 3-amino-2*H*,4*H*$^{+}$-1,2,4-triazolium 3,5-dinitrosalicylate, $C_2H_5N_4^+.C_7H_3N_2O_7^-$, (2), have been determined by X-ray diffraction and refined to residuals R = 0.035 and 0.037 for 1355 and 826 observed reflections, respectively. In both adducts, the acid protonates the hetero N atom of the amitrole ring. For (1), both molecules are involved in a network structure in which all available proton-donor and acceptor atoms, including the nitro O atoms, participate in hydrogen bonding. For (2), the two-dimensional sheet

† Part 22: Smith, Lynch, Byriel & Kennard (1995*a*).