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**The Crystal and Molecular Structure of an Asymmetric Diacetylene Monomer,
6-(2-methyl-4-nitroanilino)-2,4-hexadiyne-1-ol**

by

Marcus Vlasse* and Mark S. Paley†
Space Science Laboratory, NASA Marshall Space Flight Center
Marshall Space Flight Center, AL 35812 U.S.A.

†USRA Research Scientist

Summary

The crystal and molecular structure of an asymmetric diacetylene monomer has been determined from x-ray diffraction data. The crystals, obtained from an acetone/pentane solution, are orthorhombic, $Fdd2$ with $Z = 16$ in a unit cell having dimensions of $a = 42.815(6) \text{ \AA}$, $b = 22.224(5) \text{ \AA}$, $c = 4.996(1) \text{ \AA}$. The structure was solved by direct methods and refined by least-squares techniques to an R_F of 6.4% for 988 reflections and 171 variables. The diacetylene chains are disposed in the unit cell in a complex manner in order to satisfy the hydrogen-bonding, crystal packing, and symmetry requirements of the system. The solid state polymerization mechanism is discussed with respect to the geometric disposition of the diacetylene chains. These chains are far apart and incorrectly oriented with respect to each other to permit polymerization in the crystal by means of 1,4-addition, consistent with the Baughman mechanistic model.

Introduction

Diacetylenes and polydiacetylenes ($R-C\equiv C-C\equiv C-R'$) are important technological organic materials that have shown promise as third-order nonlinear optical matrices for applications as optical switching, four-wave mixing and logic circuits (1).

The unique feature of these compounds is the solid-state polymerization (topotactic reaction) under the influences of an energetic radiation such as UV, γ -rays, and x-rays. The search for macroscopic single crystals of polymers which can be useful in the study of solid-state properties and possible applications to technological needs have been conducted for a number of years. These efforts have been mainly unsuccessful, except for the topochemical polymerization of certain conjugated compounds (2-4). Several classes of organic compounds can undergo polymerization when exposed to high-energy radiation. Such reactions provide a means of direct synthesis of highly crystalline polymers and macromolecular systems. A direct correlation has been established between the geometry and stereochemistry of the molecules in the crystal and the crystalline molecular structure of the polymer (5-7). As mentioned above, one of these reactions is the topochemical polymerization of monomer diacetylenes with conjugated triple bonds. This reaction is known to proceed as a 1,4-addition to the conjugated triple bonds. Single crystals of a number of these monomers and polymers have been studied by x-ray and neutron diffraction and Raman spectroscopy, and their stereochemistry has been established. However, not all diacetylenes polymerize readily and some do not polymerize at all. At present, no detailed approach exists that would, a priori, predict which diacetylenes will polymerize to any specific extent.

Baughman (8) advanced a phenomenological model, based on crystallographic studies and the principle of least motion, in which he specifies the stereochemical criteria governing the disposition of the molecules in the monomer crystal required in order to bring about polymerization. In such a model, the polymerization reaction is described as a rotational motion of the structural units with a specific spacing of the reactive diacetylene chains along the growth direction (some lattice vector \vec{a}) having a period d_1 and making an angle γ_1 with vector \vec{a} (see

Fig. 1). According to this theory, the ideal parameters d_2 and γ_2 have values of 5.0 Å and 13.0 Å. The reactivity of a monomer crystal would depend, therefore, on how close d_1 and γ_1 are to d_2 and γ_2 . However, a number of other factors influence reactivity and it is not possible to make quantitative predictions about specific compounds.

At the same time, computer modeling has been used as a means of screening potentially interesting polymerizable diacetylenes (9). These computer modeling methods make use of semiempirical molecular orbital calculations such as MNDO and AM1 (10). These models attempt to predict how a particular diacetylene monomer will pack in the crystal, which is critical to its ability to polymerize readily or not. In addition, these computations provide HOMO-LUMO bandgaps, which are of importance in predicting some of the physical and optical properties of the diacetyles. Again, these predictions are rather qualitative in nature and cannot take into account the specific arrangement that the monomer will adopt in the crystalline state.

The accurate crystal structure determination of a greater number of representative diacetylenes will go a long way toward the establishment of a more accurate model which will allow the prediction of diacetylene reactivity based on the nature and shape of the functional R,R' groups attached to the diacetylene backbone.

We propose, therefore, a crystal-chemical investigation of a number of diacetylenes, having important NLO properties, which will permit to establish a more accurate reactivity model and at the same time allow to determine the structure-property relationships for optical second-order or third-order NLO behavior.

Experimental Part

The synthesis of the title compound was carried out by the Cadiot-Chodkiewicz coupling of N-propargyl-2-methyl-4-nitroaniline with bromopropargyl alcohol, as described previously (11). The pure compound is a yellow powder with m.p. 160-162 °C, and slowly turns to orange-red

upon exposure to light. Single crystals of this compound, suitable for x-ray analysis, were grown using the solvent vapor diffusion technique. A solution in acetone was exposed to n-pentane vapor over a period of about 3 days, upon which, long, thin, needle-shaped crystals were obtained. These crystals are stable in light and air and showed no apparent decomposition under x-ray radiation during the experiment. However, easy cleavage or splitting was observed along the needle axis when an attempt was made to cut them normal to this axis. A small needle in the form of a hexagonal cylinder (0.077 x 0.138 x 0.015 x 1.090 mm) was used for the data collection. The crystal symmetry was observed to be orthorhombic with space group Fdd2. The unit cell constants were obtained from 25 high-angle reflections refined on the diffractometer. These are: $a = 42.815(6)$, $b = 22.224(5)$, $c = 4.996(1)$ Å, $V = 4753.72$ Å³, $Z = 16$, $d_{\text{calc}} = 1.365$ g/cm³, $d_{\text{exp}} = 1.33(1)$ g/cm³ (determined by pycnometry). The diffraction intensities were measured with a single-crystal diffractometer (E-N CAD4) using $\theta/2\theta$ scans and Cu k_{α} ($\lambda = 1.5418$ Å) graphite-monochromated radiation up to $2\theta_{\text{max}} = 70^{\circ}$. A total of 988 independent reflections with $I > 2\sigma(I)$ were used for the analysis. No crystal movement or decay was observed during the data collection. An analytical absorption correction was applied ($\mu = 6.43$ cm⁻¹).

The structure was solved by direct methods using MULTAN contained in the EN package of programs. Refinement by full-matrix least-squares with anisotropic thermal parameters led to a final R-factor (on F) of 6.3% and a G.O.F. = 1.669. Data were weighed using non-Poisson scheme with an instrumental uncertainty factor of 0.05. A secondary extinction correction was applied to the data (12) and the coefficient was refined to a final value of 2.658×10^{-6} . Corrections for anomalous dispersion were taken from the compilations of Cramer and Lieberman (13). The hydrogen atoms positions and their thermal factors were not refined and were fixed to those determined from difference Fourier. A final Fourier difference map showed no electron density peaks greater than 0.30 e⁻/Å³. The final positional and thermal parameters are given in Tables 1 and 2*. ORTEP (14) diagrams of the molecule, and the contents of the unit cell, are given in Figures 2 and 3.

*A list of structure factors may be obtained from M.V.

Results and Discussion

The arrangement of the molecules in the unit cell is shown in Figure 3, and the structure of the molecule is given in Figure 2. The diagram indicates a complex molecular packing scheme dictated by the hydrogen bonding, the stereochemical requirements of the molecules and the crystal symmetry. The atoms C2-C5 which comprise the diacetylene backbone are nearly linear and even the extended chain C1-C6 is approximately linear with only a very small curvature toward the benzene ring. This linearity is a common element in all diacetylene derivatives and only the side-groups are inclined with respect to the chain to accommodate crystal packing and stereochemical requirements (7). The bond distances and bond angles are given in Table 3. The triple bonds in the diacetylene backbone (C2-C3 and C4-C5) have values which are comparable to the average $\langle C \equiv C \rangle = 1.206(4) \text{ \AA}$ and to other diacetylenes (7). As was observed in other substituted diacetylenes, the triple bonds seem to have a certain effect on the adjoining "single" bonds resulting in shortened C1-C3 = 1.436(9) \AA , C5-C6 = 1.49(8) \AA and even shorter C3-C4 = 1.367(9) \AA bonds. This is probably due to resonance effects in the triple-single bond system. All other bond distances and bond angles in the molecule conform to the general accepted values for organic compounds. The least-squares plane through the benzene ring shows an average deviation of 0.0031(50) \AA . Of the adjoining atoms to this ring only O2 shows a significant deviation of 0.157(4) \AA . The strongest cohesive forces in the crystal are due to hydrogen bonding of the type O1-H(O1).....O1 = 2.768(2) \AA , and N1-H(N1)....O2 = 3.03(2) \AA . Several weaker intermolecular interactions of the type C-H.....O,N also seem to play a role in the crystal cohesiveness: O1 H (C11) = 2.462(4) \AA , O2.....H \bar{r} (C13) = 2.803(4) \AA , O3.....H(O1) = 2.72(6) \AA , N2.....H \bar{r} (C13) = 2.691(5) \AA , O3.....H \bar{r} (C1) = 2.993(5) \AA , O3.....H \bar{r} (C13) = 2.979(4) \AA .

As a whole the relative disposition of the diacetylene backbone chains in the crystal does not correspond to the conditions necessary for the lattice controlled topochemical solid state polymerization of diacetylenes in crystals. These conditions formulated by Baughman (8) imply that (1) vector between the centroids of the adjacent parallel diacetylene chains should be equal to $d_1 = 4.8 - 5.6 \text{ \AA}$ and (2) the angle γ_1 between this vector and the diacetylene chain should be

about 45° (see Figure 1). Indeed, no significant polymerization seem to take place under UV, visible or x-ray irradiation of this particular compound in accordance to the Baughman conditions.

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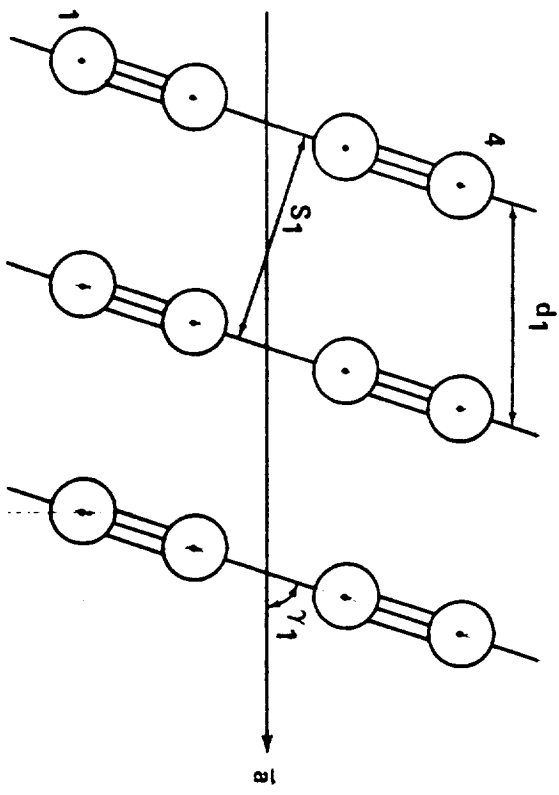
Figure Captions

Figure 1. Disposition of the diacetylene chains in the monomer and polymer crystals. The parameters d_1 and γ_1 are geometric factors for solid state polymerization.

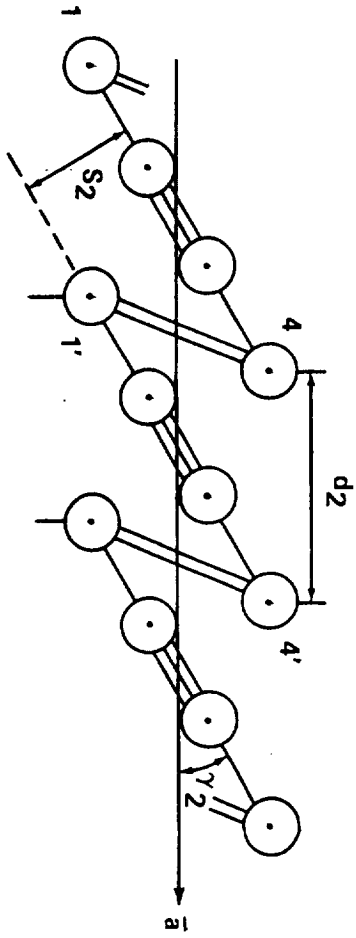
Figure 2. Stereochemical structure of the molecule.

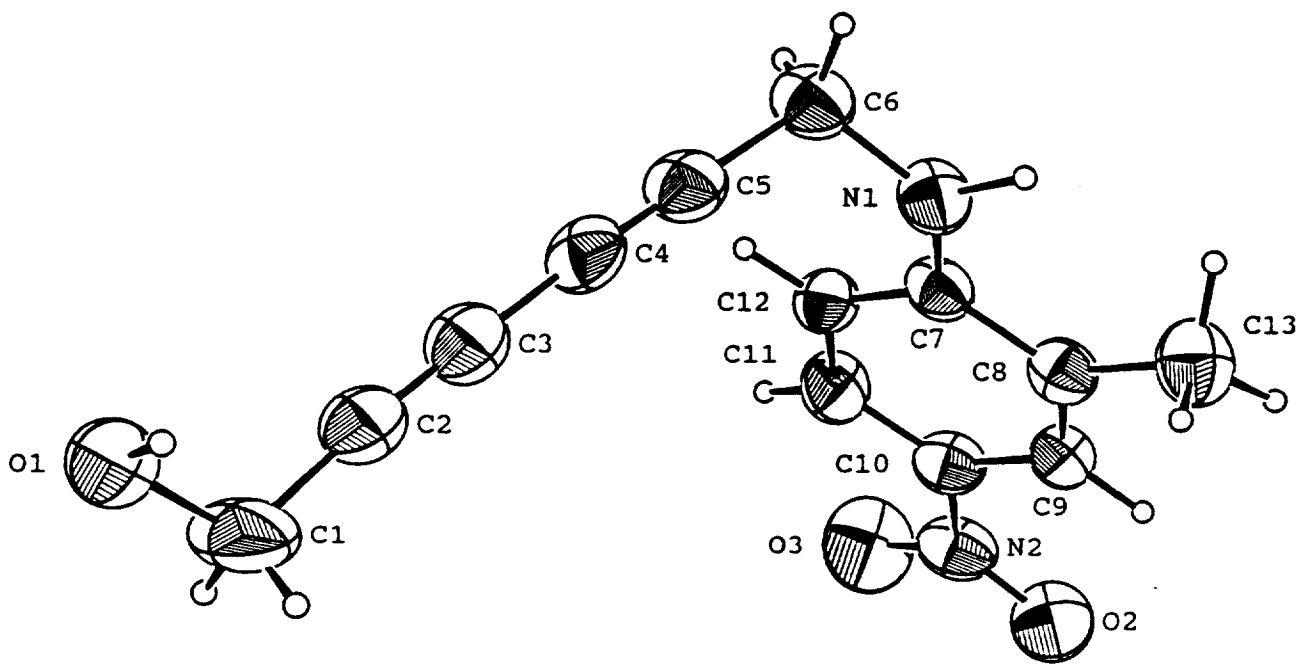
Figure 3. Arrangement of the diacetylene chains in the unit cell (dotted lines indicate hydrogen bonds).

MONOMER



POLYMER





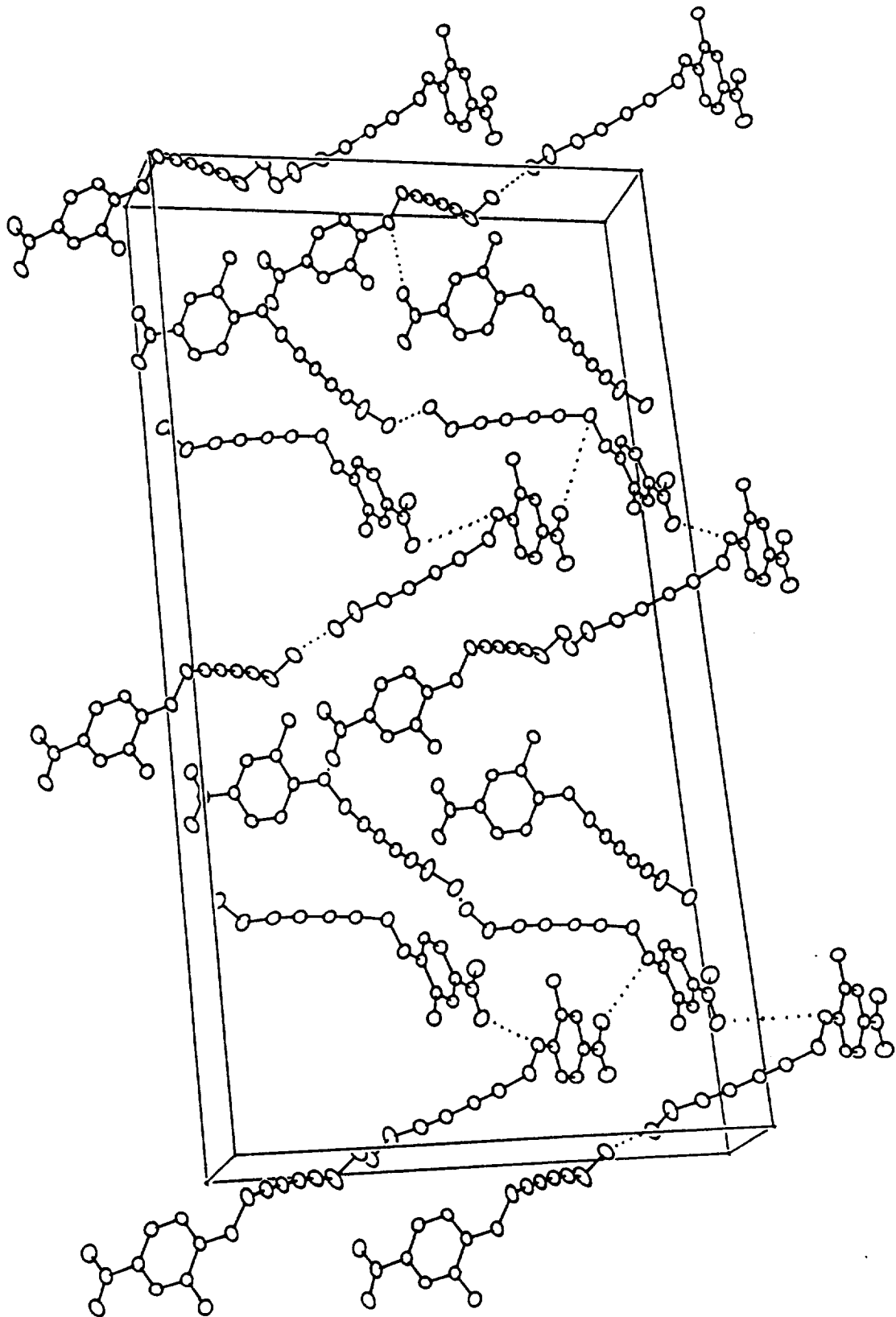


Table 1. Positional Parameters and Their ESDs for C13N2O3H12

Atom	x	y	z	B(A ²)
----	-	-	-	-----
O1	0.7527(1)	0.4737(2)	0.805(1)	5.4(1)
O2	0.8744(1)	-0.0001(2)	0.855(1)	5.09(9)
O3	0.8247(1)	-0.0038(2)	0.917(1)	6.4(1)
N1	0.83308(9)	0.1926(2)	0.017(1)	3.67(8)
N2	0.8478(1)	0.0160(2)	0.799(1)	3.96(9)
C1	0.7730(2)	0.4284(3)	0.873(2)	6.7(2)
C2	0.7762(1)	0.3839(2)	0.667(1)	4.6(1)
C3	0.7808(1)	0.3447(2)	0.503(1)	4.1(1)
C4	0.7879(1)	0.3035(2)	0.309(1)	3.8(1)
C5	0.7943(1)	0.2660(2)	0.152(1)	4.0(1)
C6	0.8041(1)	0.2211(2)	-0.053(1)	4.2(1)
C7	0.8362(1)	0.1484(2)	0.209(1)	3.02(9)
C8	0.8659(1)	0.1238(2)	0.256(1)	3.11(9)
C9	0.8690(1)	0.0806(2)	0.449(1)	3.18(9)
C10	0.8432(1)	0.0611(2)	0.597(1)	3.30(9)
C11	0.8141(1)	0.0855(2)	0.551(1)	3.8(1)
C12	0.8105(1)	0.1288(2)	0.362(1)	3.19(9)
C13	0.8938(1)	0.1437(2)	0.099(1)	4.3(1)
H(N1)	0.851(1)	0.208(2)	-0.109(13)	4.8(9)
H(O1)	0.769(1)	0.508(3)	0.673(19)	7.1(9)
H(C1)	0.766	0.410	1.034	8.3*
H'(C1)	0.793	0.446	0.902	8.3*
H(C6)	0.788	0.191	-0.068	5.5*
H'(C6)	0.806	0.241	-0.221	5.5*
H(C9)	0.889	0.064	0.484	4.2*
H(C11)	0.797	0.072	0.650	4.9*
H(C12)	0.791	0.146	0.333	4.2*
H''(C13)	0.888	0.148	-0.084	5.6*
H(C13)	0.910	0.114	0.116	5.6*
H'(C13)	0.901	0.181	0.165	5.6*

 Starred atoms were not refined but were placed in their calculated positions.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$$(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos \gamma)*B(1,2) + ac(\cos \beta)*B(1,3) + bc(\cos \alpha)*B(2,3)].$$

Table 2. Anisotropic Thermal Parameters (betas) for C13N2O3H12

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
O1	0.00085(3)	0.00280(9)	0.046(2)	0.00108(8)	-0.0020(5)	-0.0026(9)
O2	0.00081(3)	0.00246(8)	0.045(2)	0.00062(8)	-0.0000(5)	0.0073(8)
O3	0.00099(3)	0.0031(1)	0.058(2)	-0.0003(1)	0.0036(5)	0.0149(8)
N1	0.00059(2)	0.00177(7)	0.032(2)	0.00034(7)	0.0010(4)	0.0035(8)
N2	0.00077(3)	0.00170(7)	0.029(2)	-0.00001(8)	-0.0008(4)	0.0038(8)
C1	0.00131(5)	0.0029(1)	0.048(3)	0.0018(1)	-0.0078(7)	-0.006(1)
C2	0.00068(3)	0.0024(1)	0.040(3)	0.0007(1)	-0.0022(6)	0.002(1)
C3	0.00058(3)	0.00194(9)	0.041(3)	0.00026(9)	-0.0008(5)	0.002(1)
C4	0.00055(3)	0.00156(8)	0.043(3)	0.00040(8)	-0.0017(5)	0.0025(9)
C5	0.00064(3)	0.00187(9)	0.035(2)	0.00034(9)	-0.0016(5)	0.003(1)
C6	0.00077(3)	0.00177(9)	0.033(2)	0.0005(1)	-0.0008(6)	0.0022(9)
C7	0.00054(3)	0.00132(8)	0.025(2)	0.00018(8)	-0.0001(5)	-0.0007(8)
C8	0.00050(2)	0.00139(8)	0.029(2)	0.00004(8)	0.0000(4)	-0.0002(8)
C9	0.00044(2)	0.00167(8)	0.030(2)	0.00008(8)	-0.0001(4)	-0.0016(9)
C10	0.00057(3)	0.00146(8)	0.029(2)	-0.00004(8)	-0.0005(5)	0.0017(8)
C11	0.00052(3)	0.0020(1)	0.036(2)	-0.00015(9)	0.0012(5)	0.002(1)
C12	0.00047(2)	0.00146(8)	0.032(2)	0.00032(8)	-0.0009(5)	-0.0007(8)
C13	0.00059(3)	0.0021(1)	0.044(3)	-0.0002(1)	0.0018(6)	0.003(1)

The form of the anisotropic displacement parameter is:

$$\exp[-(B(1,1)*h^2 + B(2,2)*k^2 + B(3,3)*l^2 + B(1,2)*hk + B(1,3)*hl + B(2,3)*kl)].$$

Table 3. Interatomic distances (Å) and angles (°) for C13N2O3H12

<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>
O1	C1	1.372(7)	C4	C5	1.178(8)
O2	N2	1.225(7)	C5	C6	1.491(8)
O3	N2	1.232(7)	C7	C8	1.404(7)
N1	C6	1.438(7)	C7	C12	1.407(7)
N1	C7	1.381(7)	C8	C9	1.368(7)
N2	C10	1.438(7)	C8	C13	1.494(7)
C1	C2	1.436(9)	C9	C10	1.394(7)
C2	C3	1.211(9)	C10	C11	1.380(7)
C3	C4	1.367(9)	C11	C12	1.359(8)

<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>
C6	N1	C7	124.6(4)	N1	C7	C12	121.4(4)
O2	N2	O3	122.3(5)	C8	C7	C12	119.9(4)
O2	N2	C10	119.3(5)	C7	C8	C9	118.5(5)
O3	N2	C10	118.4(5)	C7	C8	C13	121.4(4)
O1	C1	C2	112.7(6)	C9	C8	C13	120.1(4)
C1	C2	C3	175.0(7)	C8	C9	C10	121.0(4)
C2	C3	C4	175.2(6)	N2	C10	C9	118.7(4)
C3	C4	C5	176.5(7)	N2	C10	C11	120.8(5)
C4	C5	C6	176.3(6)	C9	C10	C11	120.4(5)
N1	C6	C5	111.5(5)	C10	C11	C12	119.6(5)
N1	C7	C8	118.7(4)	C7	C12	C11	120.5(5)

Numbers in parentheses are estimated standard deviations in the least significant digits.