

The Crystal and Molecular Structure of 5,8-Diaza-4,9-dioxotricyclo[6,3,0,0^{1,5}]undecane, a Non-Planar Tertiary Amide

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The crystal structure of 5,8-diaza-4,9-dioxotricyclo[6,3,0,0^{1,5}]undecane, C₉H₁₂N₂O₂, a molecule designed to contain a non-planar amide bond, has been determined and refined by three-dimensional least-squares techniques. The crystals are monoclinic, space group *C2/c*, *Z*=4, with *a*=12.1576 (8), *b*=7.4193 (4), *c*=10.9614 (7) Å and $\beta=118.437(6)^\circ$. The final *R* value for 868 reflections is 0.037. The standard deviations are between 0.001 and 0.002 Å for all C, N and O atom positions. The space group utilizes the twofold rotation axis of the molecule in the crystal structure. The structure solution indicates that the N atom of the amide group is pyramidal while the twist about the amide bond is 21.3°. Significant lengthening of the C–N bond in the amide group is observed.

Introduction

The structure of 5,8-diaza-4,9-dioxotricyclo[6,3,0,0^{1,5}]undecane (DDTU) was determined as the first of a series of molecules designed to contain non-planar amide bonds. This series of tricyclic and tetracyclic amides is illustrated in Fig. 1. The synthesis of DDTU, along with several other tricyclic and tetracyclic analogs, has been reported and a correlation has been shown between the wave number $\nu(\text{C}'\text{--N})$ and the *cis* rotation angle, $\omega(\text{C}^\alpha\text{--N--C}'\text{--O})$, as measured from Dreiding models (Smolikova, Koblicova & Blaha, 1973). The purpose of the present investigation is to determine accurate conformational parameters for DDTU and to examine them in light of the correlation with spectroscopic data.

Experimental

Large colorless crystals of DDTU were obtained by equilibrating a saturated ethanolic solution of the compound with hexane. The crystal used for the diffraction experiment was cut to a more suitable size (0.5 × 0.1 × 0.06 mm) from one of the larger crystals.

Crystallographic data (Table 1) and integrated X-ray intensity data were collected on a Nonius CAD-4 automatic diffractometer. These 868 data, comprising all unique reflections with $2\theta < 144^\circ$, were measured using Cu *K* α radiation ($\lambda=1.5418$ Å) and θ – 2θ scan techniques. The θ scan width was calculated as $0.8 + 0.08 \tan \theta$. The maximum scan time was 180 s with 120 s used for scanning the peak and 30 s used for scanning both the high- θ and low- θ backgrounds. 77 reflections were considered indistinguishable from the background having a net count less than 1.4 times the square root of the total count. For the purposes of least-squares refinement these reflections were assigned a value equal

Table 1. Crystallographic data

C ₉ H ₁₂ N ₂ O ₂ , F.W. 180.21
Systematic absences: <i>hkl</i> , $h+k=2n+1$; $h0l$, $l=2n+1$, ($h=2n+1$); $0k0$, ($k=2n+1$)
Space group: <i>C2/c</i>
<i>a</i> =12.1576 ± 0.0008 Å
<i>b</i> =7.4193 ± 0.0004
<i>c</i> =10.9614 ± 0.0007
$\beta=118.437 \pm 0.006^\circ$
(determined by least-squares fit to the +2 θ and –2 θ values of 30 reflections at 26°C)
<i>V</i> =869.4 Å ³
<i>Z</i> =4
<i>D_c</i> =1.377 g cm ^{–3}
<i>D_o</i> =1.376 g cm ^{–3} (measured by flotation in CCl ₄ –C ₆ H ₁₂ mixture at 25°C)
<i>F</i> (000)=384

to 0.63 times the square root of the total count. Lorentz, polarization and absorption corrections ($\mu=8.25$ cm^{–1}) were applied. For the absorption corrections, the program of Coppens, Leiserowitz & Rabino- vich (1965) was used. The program employs the numerical integration method of Gauss, and in this case 216 sampling points were used. The weight assigned to each structure amplitude (w_F) is given by $w_F=1/\sigma_F^2$

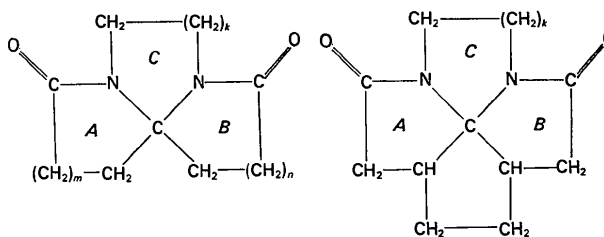


Fig. 1. Schematic structures of a series of tricyclic and tetracyclic non-planar amides. DDTU is the tricyclic compound with $k=m=n=1$.

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where σ_F is the standard deviation of the structure factor. The value of σ_F is calculated as:

$$\sigma_F = 1/2 \left(\frac{\sigma^2 + (0.05P)^2}{(P)(Lp)} \right)^{1/2}$$

where $\sigma = T^{1/2}v$, v = scan speed, $T = Pk + 2(R + L)$, $P = [Pk - 2(R + L)]v$, Pk = peak count, R = right background count, L = left background count, Lp = Lorentz-polarization factor.

Structure determination and refinement

The intensities were placed on an absolute scale using the results of a Wilson plot and normalized structure factors, $|E|$, were derived. The E statistics indicated a center of symmetry and the space group was assigned as $C2/c$ rather than Cc . The signs for 117 individual $|E|$'s greater than 1.5 were derived using the symbolic addition procedure for centrosymmetric space groups (Karle & Karle, 1966) leading to an E map that revealed the seven non-hydrogen atom positions.

The initial structure factor calculation had an $R = (\sum ||kF_o| - |F_c|| / \sum |kF_o|)$ of 0.34. The structure was refined by block-diagonal least-squares methods in which the quantity $\sum w_F (|kF_o| - |F_c|)^2$ was minimized. All non-hydrogen atoms were given anisotropic temperature factors. After several cycles of least-squares refinement R decreased to 0.10. At this point a difference map yielded the positions of the six hydrogen atoms. The hydrogen atoms were included in the refinement with isotropic temperature factors. After several further cycles of refinement inspection of observed and calculated structure factors revealed the presence of secondary extinction effects. The observed intensities were corrected for secondary extinction as follows:

$I_c = I_o \exp [-(\text{CEXT} \times \text{NET COUNT})]$ where I_c is the corrected intensity, I_o is the observed intensity and $\text{CEXT} = -2.91 \times 10^{-8}$. Least-squares refinement was terminated when the shifts for all non-hydrogen atom parameters were less than $\frac{1}{8}$ of the corresponding standard deviation. The R value based on final parameters (Tables 2 and 3) is 0.037 for all data.

Atomic scattering factors for C, N and O atoms were taken from *International Tables for X-ray Crystallography* (1962). The scattering factors for hydrogen atoms were those of Stewart, Davidson & Simpson (1965). A logical routine (Van der Helm & Nicholas, 1970), which may exclude certain reflections from least-squares refinement, was used during the refinement. A

Table 3. Positional parameters and isotropic temperature factors for hydrogen atoms (standard deviations in parentheses)

	x	y	z	B (\AA^2)
H(C2)A	0.041 (2)	0.683 (2)	0.373 (2)	5.3 (3)
H(C2)B	0.075 (1)	0.496 (2)	0.462 (1)	4.8 (3)
H(C3)A	0.219 (1)	0.651 (2)	0.342 (2)	5.0 (3)
H(C3)B	0.276 (1)	0.568 (2)	0.499 (2)	6.1 (4)
H(C5)A	-0.004 (1)	0.124 (2)	0.118 (2)	5.2 (3)
H(C5)B	0.117 (1)	0.059 (2)	0.264 (2)	4.9 (3)

final difference Fourier showed no peaks larger than 0.2 e \AA^{-3} . In the structure factor analysis the average value of $w_F \Delta F^2$ did not show a significant variation with either $|F_o|$ or $\sin \theta/\lambda$, validating the weighting scheme which was used.*

* The final F_o, F_c tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31094 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Positional and thermal parameters ($\text{\AA}^2 \times 10^4$) for carbon, oxygen and nitrogen atoms

Calculated standard deviations for the last digit are listed in parentheses. Thermal parameters are of the form

$$\exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.0	0.4508 (2)	0.25	374 (8)	437 (8)	457 (8)	0	236 (7)	0
C(2)	0.0757 (1)	0.5615 (2)	0.3821 (1)	474 (6)	521 (7)	533 (7)	-21 (5)	263 (6)	-100 (5)
C(3)	0.2082 (1)	0.5554 (2)	0.4003 (1)	451 (6)	532 (7)	528 (7)	-76 (5)	233 (6)	-60 (5)
C(4)	0.2126 (1)	0.3716 (2)	0.3431 (1)	383 (6)	549 (7)	453 (6)	-12 (5)	223 (5)	-9 (5)
C(5)	0.0447 (1)	0.1432 (2)	0.2189 (1)	460 (6)	460 (6)	592 (8)	6 (5)	228 (6)	-60 (5)
N	0.0935 (1)	0.3272 (1)	0.2477 (1)	384 (5)	465 (5)	460 (5)	1 (4)	219 (4)	-39 (4)
O	0.3050 (1)	0.2780 (1)	0.3747 (1)	416 (5)	731 (6)	647 (6)	81 (4)	228 (4)	-47 (5)

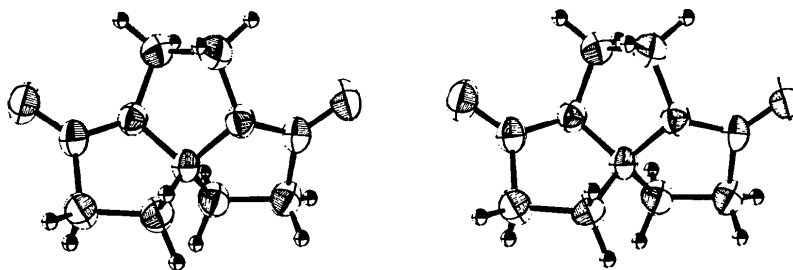


Fig. 2. Stereo view of DDTU (Johnson, 1965).

Description and discussion of the structure

A stereo view of a single molecule of DDTU is shown in Fig. 2. The molecule consists of three five-membered rings fused together at a central quaternary carbon atom. A twofold axis passes through the quaternary carbon atom and bisects the C(5)–C(5') bond of ring C. This twofold axis is a symmetry element of the space group.

All three five-membered rings are in the twist conformation. Table 4 lists the values for the torsion angles in the two types of rings together with the theoretical values for a cyclopentane ring in the twist conformation (Ouannes & Jacques, 1965). The comparison shows that both types of rings are flattened compared with cyclopentane. This can be attributed to changes in bond distances and angles created by the presence of the two amide groups and by the tendency of these two groups to be planar.

Bond distances and angles, along with the numbering scheme for DDTU, are given in Fig. 3. Bond distances and angles involving hydrogen atoms are given in Table 5. It seems reasonable to expect the thermal ellipsoids of DDTU to be consistent with a rigid-body model for thermal motion. Such a calculation was carried out using the method of Schomaker & Trueblood (1968) with the appropriate restrictions imposed for a molecule of point symmetry C_2 . The r.m.s. ΔU_{ij} was 0.0018 Å² whereas the r.m.s. σU_{ij} from the least-squares refinement was 0.0006 Å². Because the average ΔU_{ij} is three times the average σU_{ij} we conclude that the acceptance of the rigid-body model is at the limit of statistical significance. The corrected bond distances calculated from the rigid-body model are given in Table 6. The most notable bond distances are those for the C(4)–N and C(4)–O bonds. The former is shortened while the latter is lengthened from the value expected for a normal amide bond (Marsh & Donohue, 1967). The bond distances will be discussed later in the text.

One very short intermolecular contact was observed in the crystal structure. This weak interaction occurs between O and H(C3)A related by the symmetry operation $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$. The calculated distances are 3.374 Å for O...C(3) and 2.44 Å for O...H(3), both shorter than the sum of the corresponding van der Waals radii of 3.4 and 2.6 Å, respectively.

The non-planar amide group

The primary reason for the structural investigation of DDTU was to obtain conformational parameters for

the amide groups in this molecule. The conformation of the amide bond is determined by the conformations of rings A, B and C. By changing the ring size of A, B and C it is possible to produce various conformations

Table 5. Bond lengths and angles involving hydrogen atoms

Standard deviations are 0.02 Å for bond lengths and 1° for bond angles.

C(2)–H(C2)A	0.98 Å	C(1)–C(2)–H(C2)A	111°
		C(3)–C(2)–H(C2)A	114
C(2)–H(C2)B	1.00	C(1)–C(2)–H(C2)B	108
		C(3)–C(2)–H(C2)B	108
C(3)–H(C3)A	1.01	C(2)–C(3)–H(C3)A	110
		C(4)–C(3)–H(C3)A	109
C(3)–H(C3)B	1.00	C(2)–C(3)–H(C3)B	114
		C(4)–C(3)–H(C3)B	111
C(5)–H(C5)A	0.99	N—C(5)–H(C5)A	110
		C(5')–C(5)–H(C5)A	109
C(5)–H(C5)B	0.99	N—C(5)–H(C5)B	108
		C(5')–C(5)–H(C5)B	115

Table 6. Bond distances corrected for rigid-body thermal motion

	Uncorrected	Corrected
C(1)–C(2)	1.533 Å	1.538 Å
C(1)–N	1.470	1.475
C(2)–C(3)	1.526	1.530
C(3)–C(4)	1.512	1.519
C(4)–N	1.362	1.365
C(4)–O	1.223	1.226
C(5)–C(5')	1.534	1.540
C(5)–N	1.462	1.467

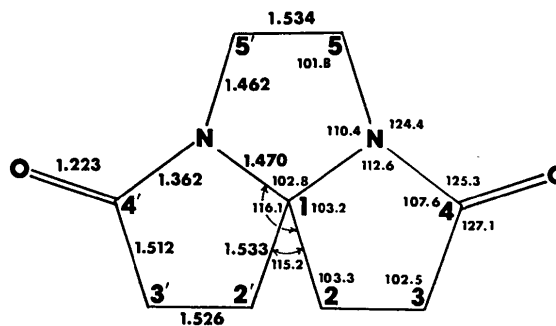


Fig. 3. Bond distances and angles for DDTU. Standard deviations for bond distances are between 0.0014 and 0.0021 Å for uncorrelated atoms and 0.0029 Å for C(5)–C(5') bond. Standard deviations for bond angles are 0.1°.

Table 4. Comparison of conformational angles (°) in five-membered rings of DDTU and theoretical values for cyclopentane (Ouannes & Jacques, 1965)

Ring A or B	Ring C	Cyclopentane
C(4)–N—C(1)–C(2)	N'—C(1)–N—C(5)	C(1)–C(2)–C(3)–C(4)
–10.7	12.1	15.1
N—C(1)–C(2)–C(3)	C(1)–N—C(5)–C(5')	C(2)–C(3)–C(4)–C(5)
26.9	–29.7	–39.4
C(1)–C(2)–C(3)–C(4)	N—C(5)–C(5')–N'	C(3)–C(4)–C(5)–C(1)
–32.6	34.8	48.1
C(1)–C(3)–C(4)–N	C(5)–C(5')–N'—C(1)	C(4)–C(5)–C(1)–C(2)
27.2	–29.7	–39.4
C(3)–C(4)–N—C(1)	C(5')–N'—C(1)–N	C(5)–C(1)–C(2)–C(3)
–10.5	12.1	15.1

of the amide group (Smolikova *et al.*, 1973). Normally the atoms of this group are planar or nearly so, but non-planarity can occur *via* three types of distortions. They are a rotation about the C'-N bond and a non-planar arrangement of bonds about either the N or C' atoms. It appears that the first two have about the same energy requirements while the last requires a relatively large amount of energy (Winkler & Dunitz, 1971). Such distortions have been observed in cyclic systems (*e.g.* Winkler & Dunitz, 1971; Sweet & Dahl, 1970; Simon, Morin & Dahl, 1972; Sletten, 1970; Groth, 1973) and also for at least one acyclic tertiary amide (Pedone, Benedetti, Immirzi & Allegra, 1970).

In order to describe the non-planarity of an amide bond three independent parameters are required. We shall follow Warshel, Levitt & Lifson (1970) in taking χ_C and χ_N to describe the non-planar arrangement of bonds about C' and N respectively. For the third parameter we shall choose τ' as defined by Winkler & Dunitz (1971). The definitions of the four torsional angles about the amide bond and their relationship to χ_N , χ_C and τ' are summarized in Table 7. It can also be seen that χ_N is the dihedral angle between the planes defined by C(4)-N-C(5) and C(4)-N-C(1) while χ_C is the dihedral angle between planes N-C(4)-O and N-C(4)-C(3). One would therefore expect the values of χ to be equal to 0 and $\pm 60^\circ$ for a planar and tetrahedral atom respectively.

Table 7. Definition of conformational parameters in the non-planar amide group (Winkler & Dunitz, 1971)

Parameter	Definition	Value for DDTU
ω_1	$\text{C}(3)\text{-C}(4)\text{-N-C}(5)$	-148.5
ω_2	$\text{O-C}(4)\text{-N-C}(1)$	169.8
ω_3	$\text{O-C}(4)\text{-N-C}(5)$	31.8
ω_4	$\text{C}(3)\text{-C}(4)\text{-N-C}(1)$	-10.5
τ'	$2\tau = \omega_1 + \omega_2$	21.3
χ_C	$\omega_1 - \omega_3 + \pi$	-0.3
χ_N	$\omega_2 - \omega_4 + \pi$	-42.0

The calculated values for the conformational parameters for DDTU are given in Table 7 from which it can be seen that the surrounding of C(4) is almost perfectly planar whereas the nitrogen atom is definitely pyramidal, in agreement with the predicted energy requirements given by Winkler & Dunitz (1971). The angle of twist (τ') about the amide bond is 21.3° . Ramachandran & Kolaskar (1973) have compiled the results of several crystal structures of non-planar peptides and shown the experimental data to be consistent with theoretical calculations (Ramachandran, Lakshminarayanan & Kolaskar, 1973). The theoretical prediction is that χ_N ($\equiv \theta_N$) has the highest probability of falling in the

range of -1.5 to -2.0 times $\Delta\omega$ ($\equiv \omega_1 + 180$). In the case of DDTU $\chi_N = -1.33\Delta\omega$, which is within the range of experimental values reported.

As the magnitude of χ_N , χ_C and τ' increases the amount of π overlap in the amide bond decreases and the amide bond length should increase. This phenomenon should be observed in the bond lengths derived from crystallographic data as well as in the infrared spectra. The amide bond length [C(4)-N] in DDTU is 1.362 ± 0.002 , about 20 standard deviations longer than the value for the standard peptide bond (Marsh & Donohue, 1967). From infrared spectra observed for DDTU and analogous compounds, the wave number $\nu(\text{C}'\text{-N})$ appears to correlate with the angle $\omega_3 = \omega\{\text{O-C}(4)\text{-N-C}(5)\}$ as estimated from Dreiding models (Smolikova *et al.*, 1973). Their estimated value of ω_3 for DDTU is 25° , somewhat smaller than the observed value of 31.8° but of the right order of magnitude.

From the results of this structure and others containing non-planar amide groups it is evident that the deformation about N provides a significant contribution to the non-planarity of the amide group and that a single rotation angle (ω_1) is not always sufficient to describe the conformation of these groups.

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Structure Cristalline du Trimétaphosphate de Baryum–Zinc Décahydraté: $\text{Ba}_2\text{Zn}(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$

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Barium zinc trimetaphosphate decahydrate, $\text{Ba}_2\text{Zn}(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$, is monoclinic, space group $C2/c$ with $Z=4$. The unit-cell dimensions are: $a=26.52(3)$, $b=7.625(5)$, $c=12.92(1)$ Å, $\beta=100.93(5)^\circ$. The crystal structure of this salt has been determined from 2898 independent reflexions collected with an automatic diffractometer. The final R value is 0.059.

Introduction

$\text{Ba}_2\text{Zn}(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$ a été préparé en utilisant la méthode décrite par Boullé (1938) pour la préparation du trimétaphosphate de calcium. Les cristaux obtenus se présentent sous la forme de prismes monocliniques aplatis suivant la direction \mathbf{a} . Le sel de baryum–cadmium est isotype. La maille de ce sel est: $a=26,52(3)$; $b=7,625(5)$; $c=12,92(1)$ Å; $\beta=100,93(5)^\circ$. Elle renferme quatre unités formulaires.

Techniques expérimentales

Le cristal utilisé pour la résolution de la structure était un fragment de prisme, approximativement cubique ($0,14 \times 0,12 \times 0,12$ mm). 2898 réflexions indépendantes ont été mesurées à l'aide d'un diffractomètre automatique Philips PW 1100 utilisant la longueur d'onde du molybdène $K\alpha_1\alpha_2$.

Aucune correction d'absorption n'a été effectuée. Le domaine angulaire exploré en balayage ω était de $1,40^\circ/\theta$. La vitesse d'exploration était de $0,04^\circ \text{ s}^{-1}$. Aucune variation significative des intensités des trois réflexions de référence n'a été observée au cours des mesures qui ont été effectuées dans un domaine angulaire s'étendant jusqu'à $30^\circ(\theta)$.

Détermination de la structure

Des investigations préliminaires d'un cristal de ce sel par la méthode de Weissenberg avaient montré que

deux groupes spatiaux étaient possibles Cc ou $C2/c$. La résolution de la structure cristalline a été conduite par des méthodes classiques. Une synthèse de Patterson révèle les atomes de baryum et de zinc; des synthèses de Fourier successives effectuées à partir des positions de ces atomes révèlent la totalité de l'arrangement atomique et confirment que le groupe spatial est le groupe centrosymétrique $C2/c$. Une série d'affinements par moindres carrés (Prewitt, 1966) conduit rapidement à un facteur $R=0,059$. A ce stade une synthèse de Fourier-différence a été effectuée pour confirmer le degré d'hydratation de ce sel.*

Description de la structure

Les atomes de zinc sont situés sur la position spéciale $4(e)$ du groupe spatial $C2/c$. Tous les autres atomes sont en position générale $8(f)$. Le Tableau 1 donne les paramètres de position et les facteurs thermiques isotropes. Le Tableau 2 donne les paramètres thermiques anisotropes. Une projection de l'ensemble des anions cycliques P_3O_9 effectuée selon la direction \mathbf{a} est donnée par la Fig. 1.

Ces anions cycliques assurent la cohésion entre les atomes de baryum situés dans des plans perpendicu-

* La liste des facteurs de structure a été déposée au dépôt d'archives de la British Library Lending Division (Supplementary Publication No. SUP 31149: 16 pp., 1 microfiche). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, Angleterre.