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Structures of the *E,Z* (*cis–trans*) Isomer of Diacetamide and the 1:1 Complex with Acetamide at 123 K. *Ab-initio* Molecular Orbital Calculations on the *Z,Z* (*trans–trans*), *E,Z* (*cis–trans*) and *E,E* (*cis–cis*) Isomers of Diacetamide

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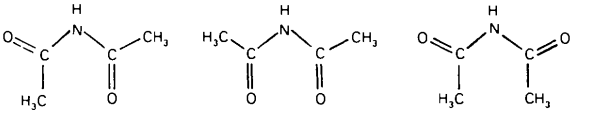
Abstract

The crystal structure of the *E,Z* (*cis–trans*) isomer of diacetamide, *N*-acetylacetamide, $C_4H_7NO_2$, has been refined using X-ray diffractometer data at 123 K. The crystal data are $P2_1/n$, $Z = 4$, $a = 4{\cdot}069$ (1), $b = 16{\cdot}818$ (5), $c = 7{\cdot}604$ (2) Å, $\beta = 94{\cdot}10$ (3)°. The final agreement factors are $R(F) = 0{\cdot}050$, $wR(F) = 0{\cdot}041$ and $S = 1{\cdot}40$ with 1384 observed reflections. The structure is disordered with an 8·2% minor component in which the molecules are appoximately related to those in the major site by a 180° rotation about the N1—C2 bond followed by a 51° rotation in the mean molecular plane about an axis through the central N atom. The crystal structure of the 1:1 complex of (*E,Z*)-diacetamide with acetamide, $C_4H_7NO_2.C_2H_5NO$, is monoclinic, $P2_1/m$, $Z = 2$, $a = 7{\cdot}695$ (9), $b = 6{\cdot}443$ (8), $c = 8{\cdot}918$ (9) Å, $\beta = 108{\cdot}90$ (9)° at 123 K. The structure was solved by direct methods and refined to $R(F) = 0{\cdot}059$, $wR(F) = 0{\cdot}049$, $S = 1{\cdot}61$ with 1275 observed reflections. *Ab-initio* molecular orbital calculations at the HF/3-21G level gave energies for the *Z,Z* (*trans–trans*) and *E,E* (*cis–cis*) isomers of diacetamide of 24·6 and 45·8 kJ mol^{-1} respectively higher than that of the most stable *E,Z* isomer. The largest difference in calculated bond lengths between the isomers was 0·014 Å between the C—N bonds in the *E,Z* and *Z,Z* isomers. The theoretical calculations indicate that the significant differences in the C—N and C=O bond lengths observed in the crystal structures of diacetamide and acetamide are due, in part, to the differences in intermolecular hydrogen bonding of the NH, NH_2 and C=O groups.

Introduction

The stereoisomers of diacetamide, *N*-acetylacetamide, $(CH_3CO)_2NH$, *E,Z* (*cis–trans*), (I), and *Z,Z* (*trans–trans*), (II), form monoclinic and orthorhombic crystals respectively. Their crystal structures were determined by Kuroda, Taira, Uno & Osaki (1975*a*,*b*). The *E,E* (*cis–cis*) isomer, (III), has not been reported.



(I) (II) (III)

Since the original X-ray crystal structure analysis of (*E,Z*)-diacetamide by Kuroda *et al.* (1975*b*) was based on photographic film data and refined to $R = 0{\cdot}167$, we have refined this crystal structure using low-temperature X-ray diffractometer data. In the course of attempting to grow larger crystals of diacetamide for neutron diffraction, we obtained crystals of the 1:1 complex of the *E,Z* isomer and acetamide. We determined and refined this crystal structure also, using low-temperature X-ray diffractometer data. Hydrogen bonding in the crystalline state has been shown to produce small but observable differences in C—NH, C—NH_2 and C=O bond lengths (Jeffrey, 1984, 1985). In an attempt to distinguish between bond-length differences which are intrinsic to the different electronic structures of these molecules and those due to crystal-field environment, we have carried out *ab-initio* MO geometry optimization calculations of the three isomers of diacetamide.

Experimental

Suitable crystals of (*E,Z*)-diacetamide were obtained by recrystallization from anhydrous dimethyl ether of a sample from Aldrich Chemical Company. Crystals of the 1:1 complex between (*E,Z*)-diacetamide and acetamide were obtained by sublimation of the diacetamide crystals in a sealed tube over a period of several weeks at room temperature. The crystal structure analysis data for both compounds are given in Table 1.

A redetermination of the crystal structure of (*E,Z*)-diacetamide by the direct method using *MITHRIL* (Gilmore, 1983) confirmed the non-H-atom atomic coordinates given by Kuroda *et al.* (1975*b*). All the H atoms were located on a difference synthesis. A further difference synthesis calculated at $R(F) = 0{\cdot}075$

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Table 1. *Crystal structure and refinement data at 123 K*

	(*E*,*Z*)-Diacetamide	(*E*,*Z*)-Diacetamide–acetamide 1:1 complex
Formula	$(CH_3CO)_2NH$	$(CH_3CO)_2NH.CH_3CONH_2$
Space group	$P2_1/n$	$P2_1m$
Z	4	2
Cell dimensions (123 K)		
a (Å)	4·069 (1)	7·695 (9)
b (Å)	16·818 (5)	6·443 (8)
c (Å)	7·604 (2)	8·918 (9)
β (°)	94·10 (3)	108·90 (9)
No. of reflections	42	39
θ range (°)	16–23	12–21
D_x (g cm^{-3})	1·29	1·27
μ(Mo $K\alpha$) (cm^{-1})	1·12	1·10
Crystal dimensions (mm)	0·24 × 0·44 × 0·48	0·12 × 0·35 × 0·47
Diffractometer	Nonius CAD-4	Nonius CAD-4
Radiation	Mo $K\alpha$ (Nb filter)	Mo $K\alpha$ (Zr filter)
Wavelength (Å)	0·7107	0·7107
Max. 2θ (°)	23	21
Standard reflections	3	3
No. of reflections measured	2291	3780; 1975 unique
No. of unobserved reflections [$I < \sigma(I)$]	907	1381; 700 unique
Range h, k, l	0→6, 0→27, −12→12	−12→11, −10→10, 0→14
Absorption, extinction corrections	None	None
Structure solution (*MITHRIL*, 250 *E* values)	>1·22	>1·17
Structure refinement (*UPALS*)	$\sum[w(k\lvert F_o\rvert - \lvert F_c\rvert)^2]$ $w^{-1} = [\sigma^2(F_o^2) + (0{\cdot}02F_o^2)]/4F_o^4$	
Atomic scattering factors	*International Tables for X-ray Crystallography* (1974)	
$R(F)$, $wR(F)$, S	0·050, 0·041, 1·40	0·059, 0·049, 1·61
Final shifts/e.s.d.	<0·1	<0·1

revealed three peaks with significant heights of 1·0, 0·7 and 0·6 e Å^{-3} in the plane of the molecule. This difference map, shown in Fig. 1(*a*), was interpreted as evidence of an alternative position of the diacetamide molecule, approximately related to the molecule in the first (major) site by a 180° rotation about the N1—C2 bond followed by a 51° rotation in the mean molecular plane about an axis through the central N atom. Fig. 1(*b*) shows the difference map after refining the occupancy factors of the molecules in each site. The molecule in the second, minor, site was included in the refinement with its molecular geometry and thermal parameters constrained to be the same as that in the major site. The sum of the occupation factors was constrained to unity. The refinement was carried out by modifying the program *UPALS* (Lundgren, 1979) to constrain the dimensions of the minor component to the same as the major component. The refinement data are included in Table 1. In the final stage of the refinement, the positional and anisotropic thermal-motion parameters of the resolved atoms of the minor component, *i.e.* C2′, C3′ and O3′, were unconstrained. No H atoms were included for the molecule in the minor site. The refined occupancy factors were 0·918 (2) and 0·082 (2). The atomic notation and thermal ellipsoids are shown in Fig. 2. The atomic parameters are given in Table 2.*

* Lists of anisotropic thermal parameters and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44880 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The structure of the (*E*,*Z*)-diacetamide–acetamide complex was solved by the direct method using *MITHRIL* (Gilmore, 1983) from 250 *E* values greater than 1·17. The *E* map for the best solution revealed all non-H-atom positions. All H-atom positions were located on difference syntheses and the parameters refined normally. The refinement converged at $R(F) = 0{\cdot}059$ and the final difference map had no significant

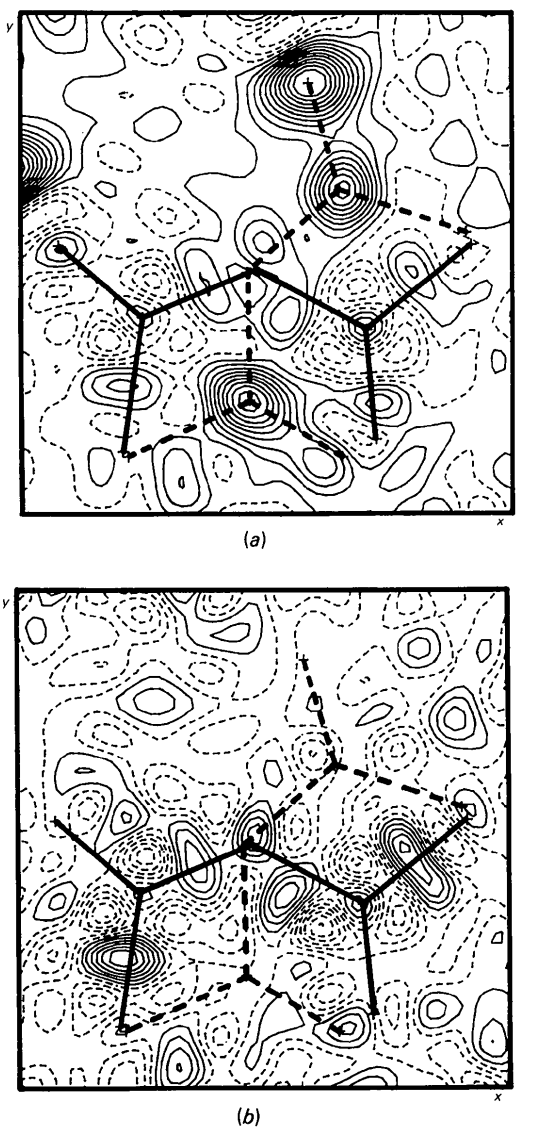

Fig. 1. Difference electron density maps for (*E*,*Z*)-diacetamide in the least-squares plane through the non-H atoms of the dimer in site 1. (*a*) After refinement giving full occupancy to site 1 [$R(F) = 0{\cdot}075$]; contour levels are 0·08 Å^3 apart between −0·28 and 0·84 Å^3. (*b*) After refinement with molecules occupying both site 1 (drawn with full lines) and site 2 (drawn with dashed lines) [$n_1 = 0{\cdot}918$ (2), $R(F) = 0{\cdot}050$]; contour levels are 0·04 Å^3 apart between −0·26 and 0·22 Å^3. Positive electron density contours are represented by full lines and negative contours by broken lines.

features. The structure analysis data are given in Table 1. The atomic notation and thermal ellipsoids are shown in Fig. 3. The atomic parameters are given in Table 3.

Discussion

The molecular dimensions

In the crystal structure of the diacetamide–acetamide complex, both molecules have crystallographic *m* symmetry, in the space group $P2_1/m$. There was no evidence from the results of the structure refinement to indicate lower symmetry.

In the (*E,Z*)-diacetamide structure, molecular *m* symmetry is not a requirement. There is a small twist at the central N atom, N1, in the direction so as to increase the O2···C5 separation. The angle between the N1,C2,O2 and N1,C3,O3 planes is 3·3 (1)°. The pyramidalization at C2 and C3 is negligible, 0·57 (21) and −0·25 (22)°. The major and minor components are almost coplanar with an angle between the least-squares planes of 1·1 (5)°.

The bond lengths and angles for (*E,Z*)-diacetamide alone and in the complex and for acetamide in the complex are shown in Table 4. There are small differences, exceeding 3σ, between the bond lengths in diacetamide alone and in the complex, *i.e.* N1—C2, 0·016 Å; C2—O2, 0·011 Å; and N1—C2—C4, 1·3°. These differences are comparable in magnitude to those between the two C—N and C=O bond lengths in the same crystal structure. These results are compared in Table 4 with the gas-phase electron diffraction data for (*E,Z*)-diacetamide (Gallacher & Bauer, 1975) and with those from the low-temperature neutron diffraction analysis of acetamide (Jeffrey, Ruble, McMullan, DeFrees, Binkley & Pople, 1980). Much larger differences (of −0·05, +0·02 Å respectively) are observed when the C—N and C=O bond lengths are compared with those in acetamide; both in the complex and in the separate X-ray (Ottersen, 1979) and neutron diffraction analyses (Jeffrey *et al.*, 1980) of the rhombohedral crystal structure.

To attempt to separate the intrinsic and extrinsic sources of the bond-length differences, these results are compared with the *ab-initio* molecular orbital geometry optimization calculations given in Table 5. These calculations indicate that about half (0·03 Å) of the observed difference in C—N bond lengths between (*E,Z*)-diacetamide and acetamide is a property of the isolated molecules; but no difference is predicted for the C=O bond lengths. The small differences of 0·006 Å in the two C—N bond lengths in the complex is in the

Table 2. *Atomic parameters for (E,Z)-diacetamide at 123 K*

Fractional coordinates × 10^4 for non-H atoms, × 10^3 for H atoms. $U_{eq} = \frac{1}{8}\pi^2 \sum_i \sum_j \beta_{ij} \mathbf{a}_i . \mathbf{a}_j \times 10^4$ (in Å^2) for non-H atoms, calculated from the refined anisotropic thermal parameters, $U \times 10^3$ (in Å^2) for H atoms. E.s.d. values given in parentheses refer to the least significant digit.

	x	*y*	*z*	U_{eq} or *U*
Site 1				
N1	7262 (4)	883 (1)	572 (3)	245 (3)
C2	5215 (3)	1523 (1)	114 (2)	248 (4)
O2	4126 (4)	1965 (1)	1190 (2)	366 (4)
C3	8578 (3)	644 (1)	2210 (2)	249 (4)
O3	10434 (3)	71 (1)	2281 (1)	322 (3)
C4	4526 (6)	1618 (1)	−1833 (2)	309 (5)
C5	7736 (7)	1073 (2)	3832 (3)	344 (6)
H1	803 (4)	61 (1)	−30 (2)	37 (5)
H41	258 (5)	187 (1)	−201 (2)	44 (5)
H42	625 (5)	189 (1)	−230 (2)	47 (5)
H43	440 (5)	110 (1)	−242 (3)	62 (6)
H51	543 (5)	109 (1)	388 (2)	45 (5)
H52	850 (5)	159 (1)	384 (2)	48 (5)
H53	869 (4)	79 (1)	483 (2)	45 (5)
Site 2				
N1′	7375 (31)	854 (8)	711 (21)	245 (3)*
C2′	6125 (34)	1321 (9)	2048 (18)	343 (51)
O2′	4241 (43)	1865 (9)	1718 (18)	366 (4)*
C3′	6678 (34)	876 (8)	−1091 (20)	327 (50)
O3′	8065 (29)	370 (7)	−1933 (15)	363 (40)
C4′	7321 (75)	1067 (17)	3847 (19)	309 (5)*
C5′	4387 (72)	1485 (15)	−1905 (16)	344 (6)*

*The positional and thermal parameters for this atom were refined as dependent parameters.

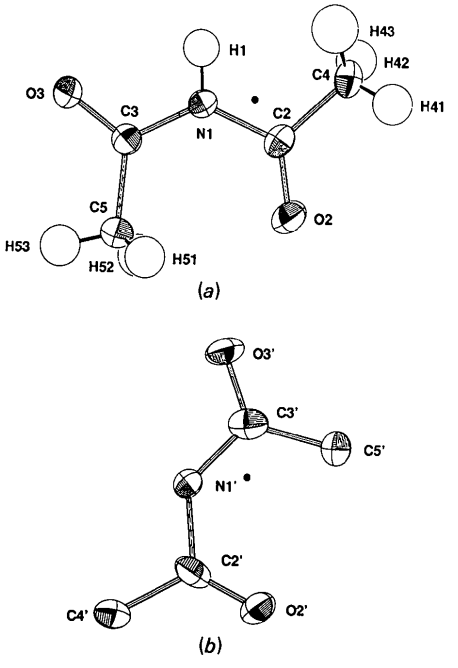

Fig. 2. *ORTEP*II (Johnson, 1976) drawings of the diacetamide molecules in (*E,Z*)-diacetamide, showing the atomic notation. (*a*) Molecule in site 1 [91·8 (2)% occupancy]; (*b*) molecule in site 2 [8·2 (2)% occupancy]. The thermal ellipsoids are drawn at the 50% probability level. The small filled circles indicate the location of a reference crystallographic inversion center, and both molecules are drawn in the same relative orientation as that in the crystal structure.

same sense, but smaller than the calculated difference. In the diacetamide structure, the difference of 0·011 Å is in the opposite sense to that calculated. The small difference in the C—C bond lengths in diacetamide corresponds to the theoretical values for the isolated molecule.

The hydrogen bonding

The three crystal structures being compared, (*E,Z*)-diacetamide, the diacetamide–acetamide complex and acetamide, use the same NH···O=C hydrogen bonds to form three different hydrogen-bonding patterns.

In the rhombohedral acetamide structure, the hydrogen bonding involves dimers which form extended nets. In the (*E,Z*)-diacetamide structure, the major components hydrogen bond to form dimers, as shown in Fig. 4(*a*). These dimers pack in staggered stacks along the *b* axis, as shown in Fig. 4(*b*). The perpendicular separation between the dimer planes in the stack is 3·23 Å. The dimers are formed by a pair of N1—H···O3=C hydrogen bonds with H···O = 1·88 (2) Å and N—H···O = 177 (2)°. The carbonyl O2 atom does not accept a hydrogen bond. The closest contacts are H41 and H42 at 2·72 (2) and 2·57 (2) Å, respectively. The minor components are also hydrogen bonded in dimers to form a pattern similar to that of the major components. There are three possible interpretations of the relationship between the major and minor components. One is that they form a separate crystal structure

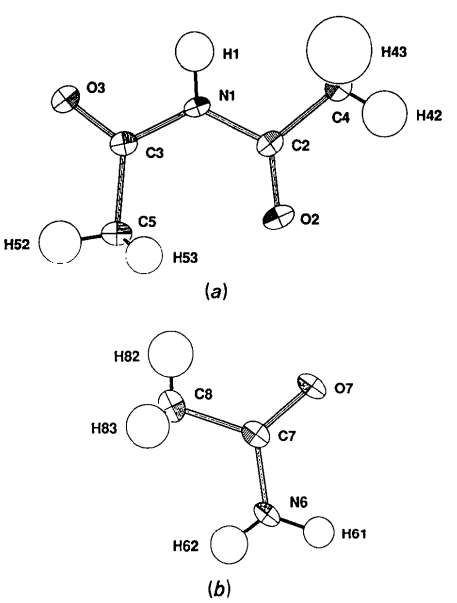

Fig. 3. *ORTEP*II (Johnson, 1976) drawings of the molecules in the complex of (*E,Z*)-diacetamide and acetamide, showing the atomic notation. (*a*) (*E,Z*)-Diacetamide, (*b*) acetamide. The thermal ellipsoids are drawn at the 50% probability level. Atoms H41, H51, H81 are directly underneath H43, H53 and H83 respectively, and are related to the latter by a mirror reflection through the plane of the molecules.

Table 3. *Atomic parameters for the crystal structure at* 123 K *of the* 1:1 *complex between (E,Z)-diacetamide and acetamide*

Fractional coordinates × 10^4 for non-H atoms, × 10^3 for H atoms. The atomic positions for atoms H43, H53 and H83 are obtained by applying the space-group symmetry operation $x, \frac{1}{2}-y, z$ to those of H41, H51 and H81, respectively. $U_{eq} \times 10^4$ (in Å^2) for non-H atoms as defined in Table 2, $U \times 10^3$ (in Å^2) for H atoms. E.s.d. values given in parentheses refer to the least significant digit.

	x	*y*	*z*	U_{eq} or *U*
Diacetamide				
N1	1313 (2)	2500	417 (2)	202 (5)
C2	1436 (3)	2500	1990 (2)	201 (6)
O2	2902 (2)	2500	3068 (2)	273 (5)
C3	2737 (3)	2500	−207 (2)	210 (6)
O3	2329 (2)	2500	−1653 (2)	310 (6)
C4	−369 (3)	2500	2282 (3)	295 (8)
C5	4679 (3)	2500	850 (3)	257 (7)
H1	18 (4)	250	−34 (3)	44 (8)
H41	−115 (4)	138 (5)	180 (3)	126 (12)
H42	−23 (4)	250	332 (4)	65 (10)
H51	489 (2)	131 (3)	153 (2)	39 (5)
H52	541 (4)	250	13 (3)	46 (8)
Acetamide				
N6	4846 (3)	2500	6449 (2)	236 (6)
C7	6678 (3)	2500	6975 (2)	217 (6)
O7	7567 (2)	2500	8411 (2)	282 (5)
C8	7614 (3)	2500	5747 (3)	277 (8)
H61	430 (3)	250	718 (3)	26 (7)
H62	430 (4)	250	551 (3)	33 (7)
H81	724 (3)	137 (4)	515 (2)	56 (6)
H82	884 (5)	250	620 (3)	53 (9)

within a minor domain; *i.e.*, a coherent twin. With more precise data, this hypothesis could be tested by comparing the results of refinements where $|F^2| = |F_{major} + F_{minor}|^2$ *versus* $|F^2| = |F_{major}|^2 + |F_{minor}|^2$. A second is that the minor component dimers are point defects in the crystal structure of the major component. This would give rise to minor to major non-H distances as short as 3·13 Å (Fig. 5). This is shorter than the minimum distance of 3·42 Å for the intermolecular distances for the major component also. A third interpretation, in which the stacks of minor components pack alongside stacks of major components in the appropriate ratio, would seem to be the most plausible model for the disorder.

In the diacetamide–acetamide complex, the molecules are hydrogen bonded in sheets. The NH_2 group bonds to the two C=O groups of the diacetamide and the NH group of the diacetamide bonds to the C=O of the acetamide, as shown in Fig. 6. There is no dimer formation. The hydrogen-bond lengths for the diacetamide, the complex, and for acetamide are given in Table 6.

Effect of hydrogen bonding on molecular structure

The comparison of experimental data and theoretical calculations on formamide (Stevens, 1978), acetamide (Jeffrey *et al.*, 1980) and monofluoroacetamide and monomer and dimer calculations on

Table 4. *Experimental molecular dimensions of (E,Z)-diacetamide and acetamide (uncorrected for thermal motion)*

Bond lengths in Å, valence and torsion angles in degrees. E.s.d.'s given in parentheses refer to the least significant digit.

	X-ray data at 123 K				Acetamide	
	(*E,Z*)-Diacetamide (major site)	(*E,Z*)-Diacetamide (in complex)	(*E,Z*)-Diacetamide (electron diffraction)[a]	Acetamide (in complex)	Neutron data at 23 K[b]	X-ray data at 123 K[c]
N1–C2	1·391 (2)	1·375 (3)	1·402	1·334 (3)	1·335 (1)	1·336 (4)
N1–C3	1·380 (2)	1·381 (3)				
C2–O2	1·211 (2)	1·222 (3)	1·210	1·241 (3)	1·247 (1)	1·243 (4)
C3–O3	1·223 (2)	1·225 (3)				
C2–C4	1·496 (3)	1·493 (4)	1·518	1·493 (3)	1·509 (1)	1·510 (3)
C3–C5	1·489 (3)	1·486 (4)				
C2–N1–C3	129·7 (2)	127·6 (2)	129·2			
N1–C2–O2	123·2 (1)	122·9 (2)	118·8	122·0	122·3 (1)	122·3 (2)
N1–C3–O3	117·9 (1)	117·3 (2)	123·7			
N1–C2–C4	113·4 (1)	114·7 (2)	117·9	116·6 (2)	116·5 (1)	116·6 (2)
N1–C3–C5	120·6 (2)	102·7 (2)	113·0			
O2–C2–C4	123·5 (1)	122·5 (2)	123·3	121·5 (2)	121·1 (1)	121·1 (2)
O3–C3–C5	121·5 (2)	122·0 (2)	123·3			
C2–N1–C3–O3	−177·3 (2)	180				
C3–N1–C2–O2	−3·8 (3)	0				
C3–N1–C2–C4	3·0 (3)	0				
C3–N1–C3–C5	175·6 (2)	180				

References: (*a*) Gallacher & Bauer (1975), (*b*) Jeffrey *et al.* (1980), (*c*) Ottersen (1979).

Table 5. *Theoretical molecular dimensions of the diacetamide isomers and acetamide, calculated at the HF/3-21G level using GAUSSIAN82 (Binkley et al., 1981)*

Values in parentheses are from Radom & Riggs (1980) calculated with STO/3-G basis; *, values assumed; †, not an independent variable. Acetamide values calculated at HF/3-21G (Jeffrey *et al.*, 1980).

	Diacetamide isomers			
	E,Z	*E,E*	*Z,Z*	Acetamide
N1–C2	1·379 (1·428)	1·389	1·393 (1·431)	1·358
N1–C3	1·395 (1·433)	1·386 (1·434)		
C2–O2	1·212	1·213	1·204 (1·218*)	1·212
C3–O3	1·212 (1·218*)	1·214 (1·218*)		
C2–C4	1·513	1·508	1·517 (1·544*)	1·516
C3–C5	1·505 (1·544*)	1·511 (1·544*)		
C2–N1–C3	129·5 (129·0†)	138·8 (136·4†)	127·0 (125·1†)	
N1–C2–O2	123·7 (123·8)	118·0	112·1 (123·1)	122·7
N1–C3–O3	118·5	118·1		
N1–C2–C4	112·8 (112·2)	121·0	123·7 (112·6)	114·4
N1–C3–C5	108·0	122·1		
O2–C2–C4	123·5	121·0	124·2	122·9
O3–C3–C5	123·5	119·8		

Total and relative energies of the diacetamide isomers

Isomer	Symmetry	*E*(total) (Hartree)	*E*(relative) (kJ mol^{-1})
E,Z	C_s	−357·74859	0·000 (0·00)
Z,Z	C_{2v}	−357·73923	24·58 (4·19)
E,E	C_s	−357·73114	45·80 (23·61)

formamide (Jeffrey, Ruble, McMullan, DeFrees & Pople, 1981) showed that in the crystal, hydrogen bonding causes a lengthening of the C=O bonds and a shortening of the C–N bonds relative to those in the isolated molecules. In formamide, acetamide and fluoroacetamide, the shortening of the C–N bonds is −0·034, −0·021, −0·017 Å respectively. The lengthening of the C=O bonds is +0·029, +0·034, +0·028 Å respectively. The theoretical calculation (at HF/3-21G) of the formamide monomer and hydrogen-bonded dimer predicted values of −0·023 and +0·018 Å. The results from this study show very similar effects.

The short C2=O2 bond length in the diacetamide structure agrees with the theoretical value for the isolated molecule and is unchanged in the crystal since

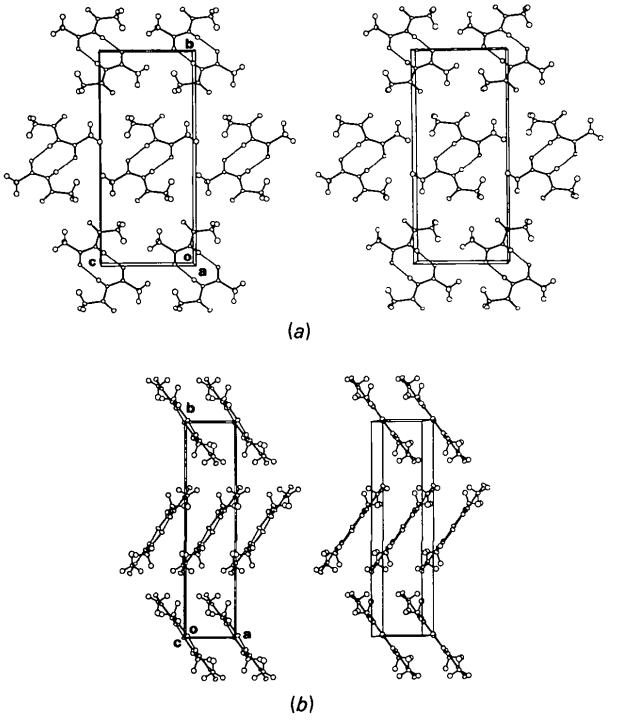

Fig. 4. *ORTEP*II (Johnson, 1976) stereoviews of the molecular packing in (*E,Z*)-diacetamide (site 1 dimers only). (*a*) Viewed down the a^* axis; (*b*) viewed down the c^* axis. Hydrogen bonds are represented by thin lines.

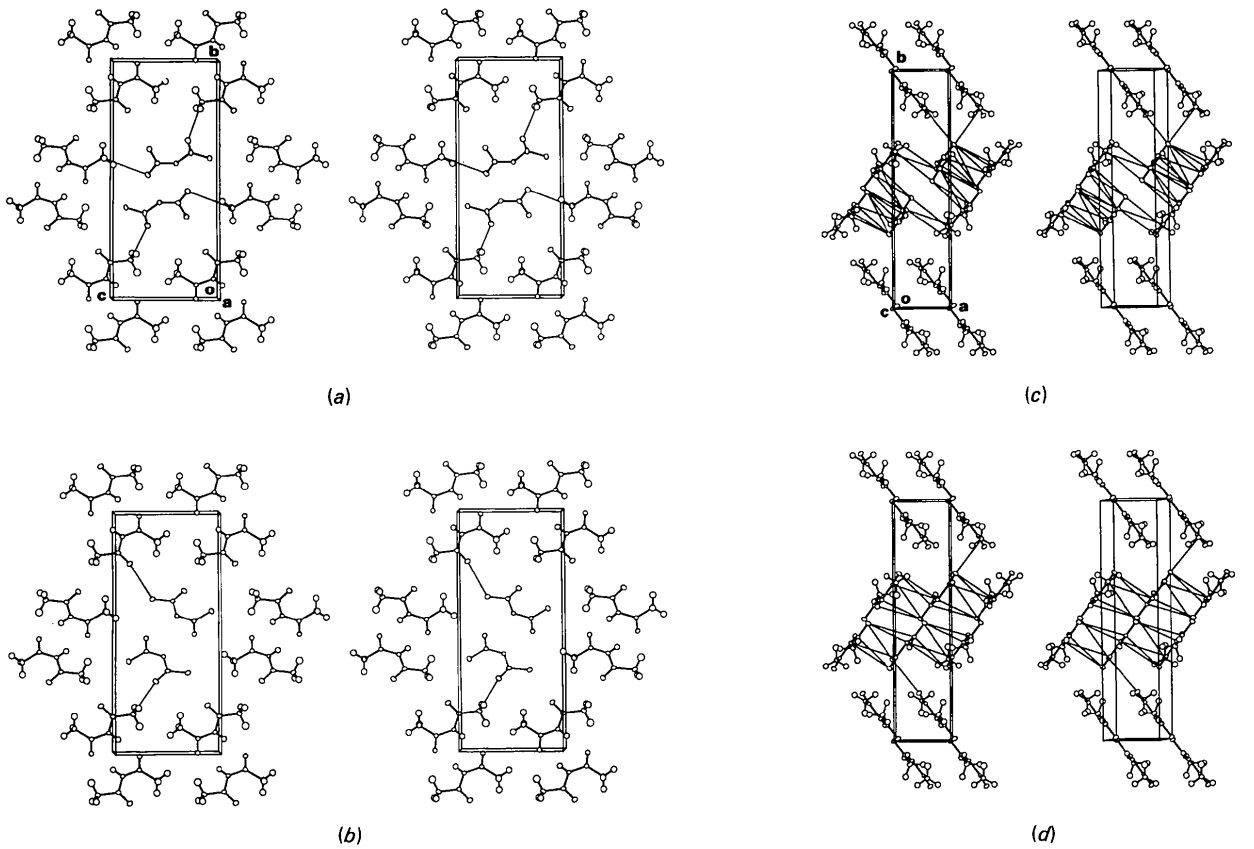

Fig. 5. *ORTEP*II (Johnson, 1976) stereoviews of the molecular packing in (*E,Z*)-diacetamide. (*a*) Viewed down the *a** axis. Dimer occupying site 2 surrounded by dimers occupying site 1. (*b*) Viewed down the *a** axis. Site 1 dimers only. (*c*) Viewed down the *c** axis. Dimer occupying site 2 surrounded by dimers occupying site 1. (*d*) Viewed down the *c** axis. Site 1 dimers only. Van der Waals contact distances between non-H atoms in the range 3·0–3·5 Å are represented by thin lines. Both distances in (*a*) are about 3·42 (2) Å, and both in (*b*) are about 3·442 (3) Å. The shortest distance is 3·128 (16) Å in (*c*) and 3·299 (2) Å in (*d*).

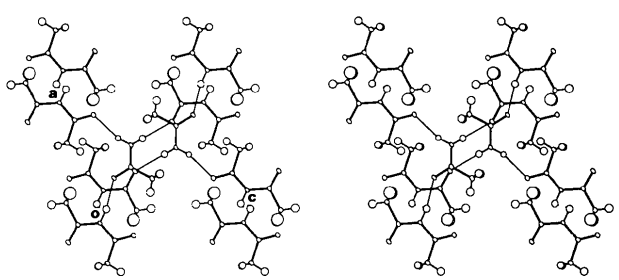

Fig. 6. *ORTEP*II (Johnson, 1976) stereoview of the molecular packing in the complex of (*E,Z*)-diacetamide and acetamide, viewed down the *b* axis. Hydrogen bonds are represented by thin lines.

Table 6. *Geometrical data for the* NH···O=C *bonds in acetamide, (E,Z)-diacetamide and the (E,Z)-diacetamide–acetamide complex*

	N–H (Å)	H···O (Å)	NH···O (°)
Acetamide (neutron data)			
N1–H1···O	1·023 (2)	1·895 (2)	167·1 (2)
N1–H2···O	1·023 (2)	1·866 (2)	171·4 (2)
(*E,Z*)-Diacetamide			
N1–H1···O3		1·88 (2)	176 (2)
(*E,Z*)-Diacetamide–acetamide complex			
(*E,Z*)-Diacetamide			
N1–H1···O7	1·030*	1·84 (3)	167 (3)
Acetamide			
N6–H61···O3	1·030*	1·96 (3)	163 (2)
N6–H62···O2	1·030*	1·87 (3)	179 (2)

* Normalized values (Taylor, Kennard & Versichel, 1984).

O2 is not a hydrogen-bond acceptor. The other C=O bond in the crystal and both bonds in diacetamide in the complex are hydrogen-bond acceptors and are increased in length by 0·012 to 0·014 Å.

Similarly the long C2–N1 bond length in the diacetamide is adjacent to the unbonded C2=O2, while all other short C–N bonds are adjacent to hydrogen-bonded C=O groups.

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Structure of 1,6-Dioxa-6a-thiapentalene, $C_5H_4O_2S$, and Comparison with a New Structure Refinement of 2,5-Diaza-1,6-dioxa-6a-thiapentalene, $C_3H_2N_2O_2S$, from X-ray and Neutron Data at 122 K. Preliminary Charge-Density Study

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Abstract

1,6-Dioxa-6a-thiapentalene (I), $M_r = 128{\cdot}1$, monoclinic, Pc, $a = 6{\cdot}774\ (5)$, $b = 3{\cdot}875\ (3)$, $c = 11{\cdot}033\ (7)$ Å, $\beta = 108{\cdot}90\ (5)°$, $V = 274\ (1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}55$ Mg m^{-3}, Zr-filtered Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}048$ mm^{-1}, $F(000) = 132$, $T = 293$ K, $wR = 0{\cdot}036$ for 731 observed reflections. 2,5-Diaza-1,6-dioxa-6a-thiapentalene (II) (new refinement at 122 K), $M_r = 130{\cdot}1$, monoclinic, $P2_1/c$, $a = 6{\cdot}836\ (3)$, $b = 6{\cdot}955\ (3)$, $c = 10{\cdot}953\ (5)$ Å, $\beta = 111{\cdot}90\ (5)°$, $V = 483\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}79$ Mg m^{-3}, Zr-filtered Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}054$ mm^{-1}, $F(000) = 264$, $T = 122$ K, $wR = 0{\cdot}044$ for 3062 reflections; neutron radiation, $\lambda = 0{\cdot}844$ Å, $\mu = 0{\cdot}07$ mm^{-1}, $wR = 0{\cdot}074$ for 1677 reflections. In both structures, as was previously observed in (II) at 293 K, the molecules are planar and have no crystallographic symmetry elements. An unusually short H···N contact of 2·30 Å is observed in (II): a corresponding C—H···N angle close to 180° suggests a weak hydrogen-bond type of interaction. Short S···O contacts of 1·83–1·88 Å, longer than the normal covalent S—O bond but much shorter than the sum of the van der Waals radii, are observed in both compounds. A preliminary experimental deformation electron density map is obtained for compound (II) from a combined X-ray and neutron

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