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The Structures of Crystals Containing *trans* and *cis* Molecules of 2,5-Dimethyl-3-hexene-2,5-diol, $C_8H_{16}O_2$, at −160°C

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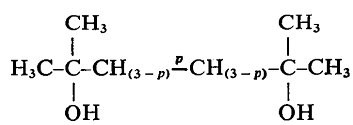
Crystals of $C_8H_{16}O_2$ have been investigated by X-ray diffraction at −160°C. Crystals of *trans*-$C_8H_{16}O_2$ have the composition $C_8H_{16}O_2.\frac{1}{2}H_2O$. The space group is *Pbcn* with $a=9{\cdot}6861$ (3), $b=10{\cdot}430$ (1), $c=18{\cdot}298$ (2) Å, $Z=8$. The structure consists of layers perpendicular to *z* in which the molecules are linked by hydrogen bonds, either directly or *via* a water molecule on a twofold axis along *z*. Crystals with space group $P\bar{1}$ with $a=8{\cdot}377$ (2), $b=13{\cdot}335$ (2), $c=6{\cdot}436$ (1) Å, $\alpha=102{\cdot}06$ (2), $\beta=74{\cdot}69$ (2), $\gamma=102{\cdot}59$ (2)°, contain two molecules of the *cis* isomer at general positions in the unit cell, and one molecule which is predominantly *trans*-$C_8H_{16}O_2$ at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. There are spirals of hydrogen bonds along *z*. The variations in the lengths of the C–C bonds (standard deviation 0·002 Å) can be ascribed to differences in hybridization and repulsion effects. Due to the repulsion, the C–C bonds in the *cis* molecules have a tendency to be longer than corresponding bonds in the *trans* molecules. The angles C=C–C are 124·9 and 127·4° in the *trans* and 132·1 and 132·5 (2)° in the *cis* molecules. No explanation has been found for the observed variation in the C–OH bond lengths from 1·432 to 1·452 (2) Å. Difference maps shows peaks lying on the centres of the C=C bonds and elongated along the normal to the plane of the central part of the molecule. No relation has been found between geometry and length of the hydrogen bonds.

Introduction

For a future accurate X-ray diffraction study of the electron density distribution in single, double and triple C–C bonds in analogous molecules, we have chosen a series of compounds derived from 2,5-dimethyl-2,5-hexanediol:



where *p* is a single, double or triple bond. First routine structure determinations at −160°C have been carried out to check whether the compounds yield crystals which are suitable for further very accurate work. The preparation of the compounds and details of the experimental work have been described in a preliminary communication (Helmholdt, Ruysink, Reynaers & Kemper, 1972). In the present paper results are given of the study of the compound with the double bond. Hereafter the molecules of the *trans* and *cis* isomers will be called II-*trans* and II-*cis*.

Crystal data and results of structure refinement

Crystals of *trans*-$C_8H_{16}O_2$ have the composition $C_8H_{16}O_2.\frac{1}{2}H_2O$. The space group is *Pbcn*, with $a=9{\cdot}6861(3)$, $b=10{\cdot}430(1)$, $c=18{\cdot}298(2)$ Å. In addition to eight II–*trans* molecules lying on general positions, the unit cell contains four H_2O molecules lying on twofold axes. The final cycles of least-squares refinement were based on 3923 independent reflexions selected from 5619 measured reflexions with $I>0$. The criteria used are $|F_o|>3w^{-1/2}$ and $|F_c|>1{\cdot}0$; the weight *w* is given by

$$w=[w_c^{-1}+0{\cdot}0002|F_o|^2]^{-1}$$

where w_c is the weight based on counting statistics. For the reflexions considered in the refinement we obtained $R=[\sum|F_o-F_c|^2/\sum|F_o|^2]^{1/2}=0{\cdot}087$ and $R_w=0{\cdot}068$. The final coordinates and thermal parameters of the carbon and oxygen atoms are listed in Tables 1 and 2. The coordinates and thermal parameters, *B*, of the hydrogen atoms are given in Table 3.

Table 1. II-*trans*.$\frac{1}{2}H_2O$. *Final coordinates of the carbon and oxygen atoms*

For numbering of atoms see the skeleton below Table 8. Standard deviations are given in parentheses in units of the last decimal place.

	x	*y*	*z*
O(1)	0·67019 (10)	0·35067 (10)	0·68368 (5)
C(2)	0·67916 (14)	0·54029 (15)	0·61254 (8)
C(3)	0·61704 (15)	0·32952 (16)	0·55508 (8)
C(4)	0·60276 (13)	0·41370 (13)	0·62261 (7)
C(5)	0·45485 (13)	0·43958 (13)	0·64472 (7)
C(6)	0·34135 (13)	0·39189 (13)	0·61468 (7)
C(7)	0·19604 (13)	0·41703 (13)	0·64151 (7)
C(8)	0·12151 (15)	0·29027 (15)	0·65578 (9)
C(9)	0·11735 (14)	0·49723 (16)	0·58540 (8)
O(10)	0·19793 (9)	0·49161 (10)	0·70747 (5)
O(11)	$\frac{1}{2}$	0·16479 (13)	$\frac{3}{4}$

During the X-ray study crystals which were expected to consist of II-*cis* molecules appeared to contain approximately one II-*trans* molecule per two II-*cis* molecules. The crystalline compound studied will be re-

Table 2. II-*trans*.$\frac{1}{2}H_2O$. *Parameters* U (Å^2)$_{ij}$ *of the temperature factor*
$\exp\,[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2klb^*c^*U_{23}+2hla^*c^*U_{13})]$

Values are $\times 10^4$.

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
O(1)	132 (4)	174 (4)	148 (4)	9 (7)	72 (7)	−49 (7)
C(2)	154 (6)	199 (6)	261 (7)	−46 (10)	128 (11)	21 (11)
C(3)	171 (6)	263 (7)	159 (6)	93 (11)	−54 (11)	44 (10)
C(4)	117 (5)	157 (6)	118 (5)	23 (9)	41 (9)	2 (8)
C(5)	115 (5)	132 (5)	132 (5)	24 (9)	10 (9)	13 (8)
C(6)	127 (5)	136 (5)	124 (5)	20 (9)	−1 (9)	6 (8)
C(7)	121 (5)	151 (5)	133 (5)	18 (9)	−34 (9)	−29 (8)
C(8)	170 (6)	200 (7)	242 (7)	−100 (11)	−19 (12)	37 (11)
C(9)	165 (6)	285 (8)	183 (6)	111 (12)	50 (12)	−71 (10)
O(10)	148 (4)	169 (4)	142 (4)	72 (8)	−60 (8)	3 (7)
O(11)	157 (6)	120 (6)	193 (6)	0	0	−77 (10)

Table 3. II-*trans*.$\frac{1}{2}H_2O$. *Final coordinates and parameters* B (Å^2) *of the hydrogen atoms*

The 'heavy' atom to which a hydrogen atom is linked is given in parentheses.

	x	y	z	B
H(O1)	0·61027	0·28372	0·70232	3·3 (5)
H(C2-1)	0·78679	0·51902	0·60302	2·7 (4)
H(C2-2)	0·66972	0·59939	0·66076	3·1 (5)
H(C2-3)	0·63877	0·59063	0·56558	3·3 (5)
H(C3-1)	0·56846	0·23710	0·56196	2·5 (4)
H(C3-2)	0·57592	0·37559	0·50689	2·3 (4)
H(C3-3)	0·72527	0·31153	0·54527	2·3 (4)
H(C5)	0·44914	0·49901	0·69231	1·4 (3)
H(C6)	0·34548	0·32770	0·56910	1·8 (4)
H(C8-1)	0·17534	0·23386	0·69627	2·7 (4)
H(C8-2)	0·11469	0·23402	0·60634	1·3 (3)
H(C8-3)	0·01884	0·31021	0·67580	3·3 (5)
H(C9-1)	0·11702	0·44911	0·53312	3·0 (4)
H(C9-2)	0·01177	0·50702	0·60355	2·2 (4)
H(C9-3)	0·16717	0·58931	0·57967	2·5 (4)
H(O10)	0·23880	0·44074	0·74622	3·8 (5)
H(O11)	0·43167	0·10809	0·73087	4·3 (5)

ferred to as II-*cis*.$\frac{1}{2}$II-*trans*. The space group of the crystals is $P\bar{1}$ with $a=8{\cdot}377(2)$, $b=13{\cdot}335(2)$, $c=6{\cdot}436(1)$ Å, $\alpha=102{\cdot}06(2)$, $\beta=74{\cdot}69(2)$, $\gamma=102{\cdot}59(2)$°. The unit cell contains two II-*cis* molecules related by an inversion centre and a third molecule at ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$). The latter molecule appeared to be a superposition of a large percentage of II-*trans* molecules and a small percentage of the analogous molecules with a single C–C bond. Out of the 8453 observed reflexions with $I>0$, 6395 reflexions were selected for the later stages of the least-squares refinement. The criteria used were $|F_o|>3w^{-1/2}$ and $|F_c|>0{\cdot}5$, w being calculated from $w=[w_c^{-1}+0{\cdot}0004|F_o|^2]^{-1}$. The final parameters are listed in Tables 4 to 6. R and R_w are both 0·074.*

The effect of the disorder in II-*cis*.$\frac{1}{2}$II-*trans* on the atomic coordinates has been examined critically. By varying the proposed disorder around ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$) so that the difference map remains flat, it could be shown that the coordinates of the II-*cis* molecules are not affected by the assumptions made for the structure around ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$). These coordinates are therefore be-

* Tables of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30439 (46 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. II-*cis*.$\frac{1}{2}$II-*trans*. *Final coordinates of the carbon and oxygen atoms*

	x	y	z
O(1)	0·51917 (9)	0·29192 (5)	0·84658 (12)
C(2)	0·73548 (14)	0·20682 (9)	0·86371 (20)
C(3)	0·65420 (15)	0·19500 (9)	0·50949 (17)
C(4)	0·58976 (12)	0·19862 (7)	0·75587 (16)
C(5)	0·46469 (14)	0·09983 (8)	0·79968 (17)
C(6)	0·32421 (14)	0·08106 (8)	0·95375 (17)
C(7)	0·23174 (13)	0·15199 (8)	1·14131 (16)
C(8)	0·15495 (16)	0·09410 (9)	1·33565 (19)
C(9)	0·09319 (15)	0·18472 (10)	1·06897 (21)
O(10)	0·34138 (10)	0·24222 (6)	1·21885 (12)
C(11)	0·44699 (19)	0·51213 (10)	0·59629 (28)
C(12)	0·28460 (12)	0·44182 (7)	0·68540 (16)
C(13)	0·14352 (17)	0·45255 (11)	0·58757 (20)
C(14)	0·23801 (16)	0·46964 (9)	0·93233 (18)
O(15)	0·30624 (10)	0·33472 (6)	0·63937 (11)

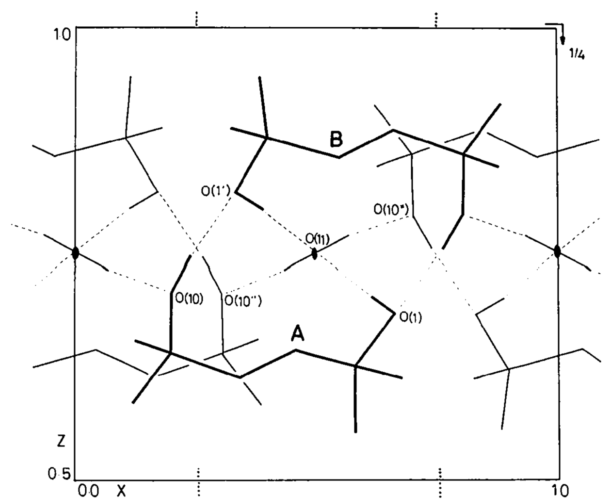


Fig. 1. II-*trans*.$\frac{1}{2}H_2O$. Projection of the structure along [010] onto the plane (010). The molecules shown by thin lines are related to those shown by thick lines by the b glide plane. O–H bonds are indicated, C–H bonds are not given.

lieved to have good accuracy, in contradistinction to those of the 'II-*trans* molecules' around ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$) for which the accuracy is low. It is interesting to note that the hydrogen-bonding system in the crystal described below is not affected by the disorder, as the geometry of the superimposed molecules is such that the OH groups of the two molecules coincide. We believe, however, that a very accurate study of II-*cis*.$\frac{1}{2}$II-*trans* crystals will be hampered by the disorder. Crystals of

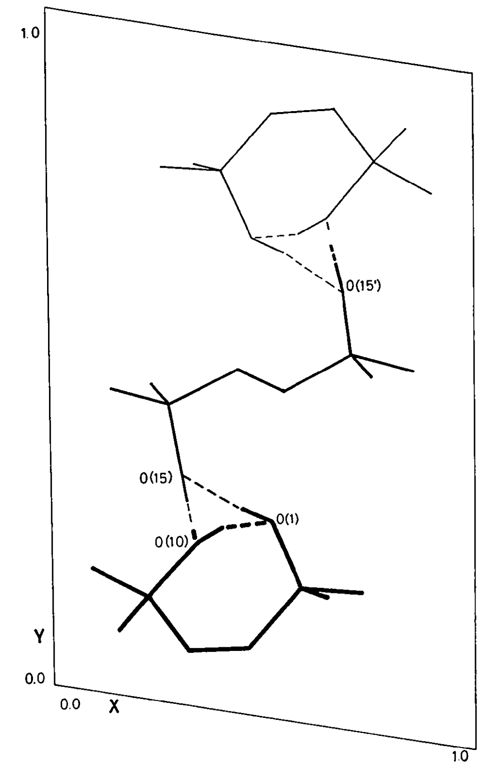


Fig. 2. II-*cis*.$\frac{1}{2}$II-*trans*. Projection of the structure along [001] onto the plane (001). The heights of the molecules decrease from II-*cis* lower part unit cell *via* 'II-*trans*' at ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$) to II-*cis* upper part unit cell.

Table 6. II-*cis*.$\frac{1}{2}$II-*trans*. *Final coordinates and parameters B of the hydrogen atoms*

	x	*y*	*z*	*B*
H(O1)	0·44528	0·30402	0·76449	5·5 (5)
H(C2-1)	0·68912	0·21218	1·03829	2·7 (4)
H(C2-2)	0·79381	0·13841	0·80506	2·7 (3)
H(C2-3)	0·83003	0·27439	0·82997	3·2 (4)
H(C3-1)	0·55123	0·18920	0·43358	2·5 (3)
H(C3-2)	0·71931	0·13023	0·43568	2·8 (4)
H(C3-3)	0·74127	0·26539	0·47467	3·0 (4)
H(C5)	0·50545	0·03441	0·68586	2·9 (4)
H(C6)	0·26376	0·00132	0·94262	2·2 (3)
H(C8-1)	0·06863	0·02452	1·29265	1·9 (3)
H(C8-2)	0·25196	0·06895	1·38409	2·9 (4)
H(C8-3)	0·09107	0·14491	1·47059	3·0 (4)
H(C9-1)	0·00594	0·11768	1·01654	2·8 (4)
H(C9-2)	0·02422	0·23455	1·20055	3·0 (4)
H(C9-3)	0·14300	0·22492	0·93007	3·2 (4)
H(O10)	0·40874	0·27310	1·09306	4·6 (5)
H(C11)*	0·4371 (22)	0·5882 (14)	0·6314 (29)	3·2 (4)
H(C13-1)	0·12073	0·53172	0·62452	4·7 (5)
H(C13-2)	0·17070	0·42473	0·41402	3·0 (4)
H(C13-3)	0·02506	0·40739	0·65739	3·1 (4)
H(C14-1)	0·12002	0·42214	0·99565	3·5 (4)
H(C14-2)	0·33269	0·45249	0·99912	3·4 (4)
H(C14-3)	0·22458	0·55051	0·98015	3·0 (4)
H(O15)	0·31687	0·30762	0·48525	2·9 (4)

* Because of the disorder of the 'II-*trans* molecule' in II-*cis*.$\frac{1}{2}$II-*trans* the coordinates of H(C11) were not fixed during the refinement.

II-*trans*.$\frac{1}{2}H_2O$ will therefore be used for the further accurate study of the double bond.

Description and discussion of the structures

The packing in the crystals of II-*trans*.$\frac{1}{2}H_2O$

The [010] projection of the structure is given in Fig. 1. The molecules are arranged in layers perpendicular to *z*. One layer consisting of II-*trans* and water molecules connected by hydrogen bonds is shown in Fig. 1. Successive layers in the *z* direction are obtained from the layer shown in Fig. 1 by the operation of the *c* glide plane. The layers are held together by van der Waals interactions only; no short intermolecular distances are present.

Table 5. II-*cis*.$\frac{1}{2}$II-*trans*. *Parameters* U_{ij}

Values are $\times 10^4$.

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
O(1)	192 (3)	135 (3)	150 (3)	80 (5)	24 (4)	−84 (5)
C(2)	207 (5)	239 (5)	284 (5)	94 (8)	80 (8)	−194 (8)
C(3)	266 (5)	240 (5)	154 (4)	137 (8)	55 (7)	26 (7)
C(4)	160 (4)	146 (4)	151 (4)	81 (6)	29 (6)	−39 (6)
C(5)	222 (4)	141 (4)	178 (4)	57 (6)	−12 (6)	−35 (7)
C(6)	223 (4)	136 (4)	185 (4)	−13 (6)	6 (6)	−54 (7)
C(7)	182 (4)	144 (4)	146 (4)	−25 (6)	27 (6)	−54 (6)
C(8)	305 (6)	213 (5)	195 (5)	−28 (8)	135 (7)	−10 (8)
C(9)	188 (5)	275 (5)	302 (5)	39 (8)	162 (9)	−115 (8)
O(10)	232 (3)	162 (3)	127 (3)	−58 (5)	−11 (4)	−80 (5)
C(11)	364 (7)	155 (5)	564 (9)	−90 (9)	−113 (10)	538 (13)
C(12)	154 (4)	135 (4)	169 (4)	55 (6)	30 (6)	−16 (6)
C(13)	318 (6)	326 (6)	248 (5)	310 (10)	88 (9)	−166 (9)
C(14)	306 (6)	232 (5)	177 (4)	180 (8)	−83 (7)	−93 (8)
O(15)	229 (3)	138 (3)	9132 (3)	96 (5)	6 (4)	−98 (5)

The hydrogen bonding within a layer can be described as follows. The molecules *A* and *B* related by the twofold axis [$\frac{1}{2}$,*y*,$\frac{3}{4}$] are directly linked by two equivalent hydrogen bonds of type O(10)–H(10)···O(1′) and indirectly *via* the water molecule by hydrogen bonds of type O(1)–H(1)···O(11)···H(1′)–O(1′). The water molecule also serves to connect the unit *A–B* *via* bonds of the type O(1)–H(1)···O(11)–H(11)···O(10*) with molecules shifted half a unit cell in the *y* direction by the *b* glide plane. Finally the water molecules take part in the extension of the hydrogen-bonding network along the *x* direction, molecule *B* being connected with *A*(*x*+1,*y*,*z*) *via* the water molecule at the twofold axis [1,*y*,$\frac{3}{4}$] with a bond of type O(10*)···H(11)–O(11)–H′(11)···O(10″).

The packing in the crystals of II-*cis*.$\frac{1}{2}$II-*trans*

Fig. 2 shows the structure of II-*cis*.$\frac{1}{2}$II-*trans* in [001] projection. The structure contains spirals of hydrogen bonds along the *z* direction. The projection of one spi-

Table 7. *Distances* (Å) *and angles* (°) *for the hydrogen bonds in* II-*trans*.$\frac{1}{2}H_2O$ (*upper three lines*) *and in* II-*cis*.$\frac{1}{2}$II-*trans* (*lower three lines*)

```
                                            C(f)
                                           /
The numbering system used is C(a)–O(b)–H(c)···O(d)    .
                                           \
                                            H(e)
```

For bonds in which the water molecule takes part either C(*a*) reads H(*a*) or C(*f*) reads H(*f*). *A* = angle between *b–d* and plane *def*, *B* = distance of *b* from plane *def*.

O(*b*)	O(*d*)	*b–d*	*c–d*	*b–c–d*	*a–b–c*	*a–b–d*	*e–d–f*	*b–d–e*	*b–d–f*	*A*	*B*
O(11)	O(10)	2·747 Å	1·799 Å	172·0°	103·4°	100·4°	108·9°	115·9°	125·8°	27·9°	1·284 Å
O(10)	O(1)	2·786	1·818	175·0	108·9	108·7	109·1	113·8	121·2	37·2	1·683
O(1)	O(11)	2·819	1·855	172·5	109·1	112·3	103·4	132·4	100·3	40·8	1·843
O(15)	O(10)	2·697	1·735	171·4	110·8	116·3	107·5	125·9	124·8	12·0	0·560
O(1)	O(15)	2·702	1·736	174·4	113·8	116·8	110·8	118·7	114·4	37·9	1·661
O(10)	O(1)	2·597	1·651	164·2	107·5	99·2	113·3	109·1	99·7	62·6*	2·305

* *A* = 0° if *b–d* bisects the angle between the lone pairs, *A* ≃ 55° (half the tetrahedral angle) if *b–d* coincides with one of the lone pairs. The value 62·6° shows that *b–d* lies outside the lone-pair region for the bond considered (the intramolecular bond in II-*cis*.$\frac{1}{2}$II-*trans*).

Table 8. *Bond lengths* (Å) *in the* II-*trans and* II-*cis molecules*

The standard deviations are 0·002 Å, except for 'II-*trans*' in II-*cis*.$\frac{1}{2}$II-*trans* where the accuracy is lower due to the disorder.

Bond type		II-*trans*	II-*cis*	Lit.	'II-*trans*'§	
C(sp^3)–C(sp^3)	C(2)—C(4)	1·525	1·530		C(13)–C(12)	1·522
	C(3)—C(4)	1·522	1·528		C(14)—C(12)	1·518
	C(8)—C(7)	1·529	1·529			
	C(9)—C(7)	1·528	1·531			
Average value		1·526	1·530	1·528*		
C(sp^3)–C(sp^2)	C(4)—C(5)	1·513	1·520		C(12)–C(11)	1·522
	C(7)—C(6)	1·514	1·517			
Average value		1·513	1·518	1·511†		
C(sp^2)–C(sp^2)	C(5)—C(6)	1·326	1·338	1·333‡	C(11′)–C(11)	1·344
	O(1)—C(4)	1·452	1·440		O(15)–C(12)	1·438
	O(10)–C(7)	1·436	1·432			

* Davis & Hassel (1963).
† Weighted average of 14 accurately determined bond lengths from *Acta Cryst.* (1971). **B27**.
‡ Bartell & Bonham (1959).
§ Numbering scheme for 'heavy' atoms:

(*a*) Molecules on general positions:

```
    O(1)               O(10)
     |                   |
C(2)–C(4)–C(5)=C(6)–C(7)–C(9)
     |                   |
    C(3)                C(8)
```

(*b*) Molecule at inversion centre in II-*cis*.$\frac{1}{2}$II-*trans*:

```
      O(15′)                    O(15)
        |                         |
C(14′)–C(12′)–C(11′)=C(11)–C(12)–C(14)
        |                         |
      C(13′)                    C(13)
```

ral is shown in the lower part of the unit cell. The spiral uses both OH groups of the II-*cis* molecule in the lower part of the unit cell and one OH group of 'II-*trans*' at ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$) in the sequence:
O(10;z–1)···H–O(15)···H–O(1)···H–O(10;z) *etc.*
The remaining OH group of II-*trans* at ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$) takes part in the centrosymmetrically related spiral shown in the upper part of the unit cell. In this way chains of type

/ /
trans
/ /
cis cis
/ /
trans
/ /
cis cis
/ /
trans
/ /

are formed in the z direction. The three molecules in Fig. 2 belong to the same chain. Successive chains in the x and y directions are linked by van der Waals interaction only: no short intermolecular distances are observed.

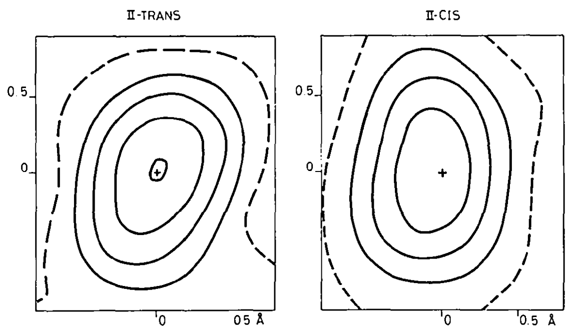


Fig. 3. Difference syntheses for the II-*trans* and II-*cis* molecules. The double bond C(5)=C(6) is perpendicular to the drawing, its centre coinciding with +. The vertical direction corresponds to the normal to the plane C(4)C(5)C(6)C(7). Contours are drawn at intervals of 0·1 e Å^{-3}, the zero line is dashed. σ=0·06 e Å^{-3}.

Geometry of the hydrogen bonds

Atomic distances and angles which are of interest for the characterization of the hydrogen bonds are given in Table 7. We see that the intramolecular hydrogen bond O(10)–H···O(1) in the II-*cis* molecules of Fig. 2 is relatively short and has the largest deviation from linearity. The intermolecular hydrogen bonds in II-*cis*.$\frac{1}{2}$II-*trans* are shorter than those in II-*trans*.$\frac{1}{2}H_2O$. No explanation for this phenomenon has been found from the geometry of the bonds. It seems that the lengths of hydrogen bonds do not only depend on their immediate surroundings but are also influenced by the crystal packing as a whole. For the bonds using the water molecules in II-*trans*.$\frac{1}{2}H_2O$, O(1)–H···O(11) with the water molecule as H-acceptor is longer than O(11)–H···O(19) with the water molecule as H-donor. In this case the geometry of the bonds may play a part. It can be deduced from the differences between *b–d–e* and *b–d–f* in Table 7 that for O(1)–H···O(11), which is the longest hydrogen bond in II-*trans*.$\frac{1}{2}H_2O$, the location of the line O···O relative to the lone pairs of O(*d*) is less favourable than for the remaining bonds in II-*trans*.$\frac{1}{2}H_2O$.

The individual molecules

Analysis of the thermal parameters according to Pawley (1963) has shown that the molecules do not behave as rigid bodies. No corrections for libration have therefore been applied to the bond lengths and angles given in Tables 8 and 9. The values given for the 'II-*trans* molecules' in II-*cis*.$\frac{1}{2}$II-*trans* will not be discussed

Table 9. *Valence angles (°) in the* II-*trans and* II-*cis molecules*

Standard deviations are 0·2°, except for 'II-*trans*' in II-*cis*.$\frac{1}{2}$II-*trans* where the accuracy is lower.

	II-*trans*	II-*cis*		'II-*trans*'
O(1)—C(4)–C(2)	105·5	106·1	O(15)–C(12)–C(14)	106·0
O(1)—C(4)–C(3)	108·8	108·8	O(15)–C(12)–C(13)	109·3
O(1)—C(4)–C(5)	107·5	113·1	O(15)–C(12)–C(11)	111·0
C(2)—C(4)–C(3)	110·9	110·4	C(14)–C(12)–C(13)	110·5
C(2)—C(4)–C(5)	109·7	109·3	C(14)–C(12)–C(11)	109·2
C(3)—C(4)–C(5)	114·0	109·1	C(13)–C(12)–C(11)	110·7
O(10)–C(7)–C(9)	105·9	110·0		
O(10)–C(7)–C(8)	109·3	105·6		
O(10)–C(7)–C(6)	110·8	112·5		
C(9)—C(7)–C(8)	110·7	110·0		
C(9)—C(7)–C(6)	109·9	109·4		
C(8)—C(7)–C(6)	110·2	109·3		
C(6)—C(5)–C(4)	127·4	132·5	C(11′)–C(11)–C(12)	124·4
C(6)—C(5)–H(C5)	120·8	117·3	C(11′)–C(11)–H(C11)	112·8
C(4)—C(5)–H(C5)	111·7	110·2	C(12)–C(11)–H(C11)	112·9
C(5)—C(6)–C(7)	124·9	132·1		
C(5)—C(6)–H(C6)	121·8	114·6		
C(7)—C(6)–H(C6)	113·3	113·2		

further as the coordinates of this molecule are not very accurate due to the disorder discussed above.

Table 8 shows that chemically equivalent C–C bonds within each of the molecules are equal within experimental error. As expected $C(sp^3)$–$C(sp^2)$ bonds are shorter than $C(sp^3)$–$C(sp^3)$ bonds. The C–C bonds in II-*cis* tend to be longer than corresponding bonds in II-*trans*. We ascribe this elongation to repulsion. No explanation has been found for the variation in C–OH bond lengths.

As observed in various other compounds, *e.g.* in 4,5-di-t-butylimidazole and 2,3-di-t-butylquinoxaline (Visser & Vos, 1971*a*, *b*), the variations in the O–C–C and C–C–C angles are large compared with their standard deviations (Table 9). Repulsion causes the angles C=C–C in the II-*cis* molecule (132·5 and 132·1°) to be considerably larger than those in the II-*trans* molecule (127·4 and 124·9°), whereas the angles C=C–C in II-*trans* are still larger than the angle C=C–C of 123° in *trans*-2-butene (Sutton, 1965, M112). The difference between the angles C=C–C in II-*trans* can also be ascribed to repulsion, as can be seen from the values of the short non-bonded distances C(3)···C(6)=2·95 Å, *i.e.* 0·45 Å shorter than the C···C van der Waals distance of 3·4 Å, and O(10)···C(5)=2·78 Å, *i.e.* 0·32 Å smaller than the O···C van der Waals distance of 3·1 Å. Consideration of the molecular skeleton at the bottom of Table 8 shows that the increase in repulsion when going from O(10)···C(5) to C(3)···C(6) causes the angle C(6)–C(5)–C(4)=127·4° to be larger than the angle C(5)–C(6)–C(7)=124·9°.

Although the structure determination is not extremely accurate as yet, it is worth studying the electron density distributions perpendicular to the double bonds of the two molecules. Therefore difference densities were calculated for sections perpendicular to these bonds. The F_c values were based on the final parameters of the structure refinement (reflexions up to $2 \sin \theta/\lambda = 1{\cdot}92$ Å^{-1}). Only reflexions up to $2 \sin \theta/\lambda = 1{\cdot}20$ Å^{-1} were included in the difference map as it was expected that for reflexions with higher $2 \sin \theta/\lambda$ values the random errors would obscure the systematic contribution to the difference density. The difference maps are shown in Fig. 3. As expected we see that the peaks showing the presence of bonding electrons in the double bonds are elongated along the normal to the plane through the double bond and its adjacent atoms. The height of the maxima are 0·44 and 0·39(6) e Å^{-3} for II-*trans* and II-*cis* respectively. This is about a factor of two lower than the values which we have obtained from theoretical calculations for C–C bonds in molecules subject to thermal vibrations (Ruysink & Vos, 1974*a*). The reduction of the height of the maxima has been discussed in another paper (Ruysink & Vos, 1974*b*). Moreover in the future more accurate intensity measurements will be made, preferably at He temperatures, to obtain more detailed information on the electron density distribution in the double bond. For this work crystals of II-*trans*.$\frac{1}{2}H_2O$ will be used.

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References

BARTELL, L. S. & BONHAM, R. A. (1959). *J. Chem. Phys.* **31**, 400–404.

DAVIS, M. & HASSEL, O. (1963). *Acta Chem. Scand.* **17**, 1181.

HELMHOLDT, R. B., RUYSINK, A. F. J., REYNAERS, H. & KEMPER, G. (1972). *Acta Cryst.* B**28**, 318–319.

PAWLEY, G. S. (1963). *Acta Cryst.* **16**, 1204–1208.

RUYSINK, A. F. J. & VOS, A. (1974*a*). *Acta Cryst.* A**30**, 497–502.

RUYSINK, A. F. J. & VOS, A. (1974*b*). *Acta Cryst.* A**30**, 503–506.

SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions*, Supplement 1956–1959. London: The Chemical Society.

VISSER, G. J. & VOS, A. (1971*a*). *Acta Cryst.* B**27**, 1793–1801.

VISSER, G. J. & VOS, A. (1971*b*). *Acta Cryst.* B**27**, 1802–1811.