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The Crystal Structure of Methixene Hydrochloride Monohydrate

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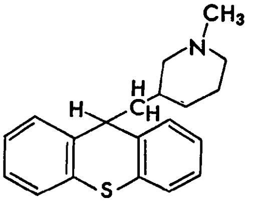
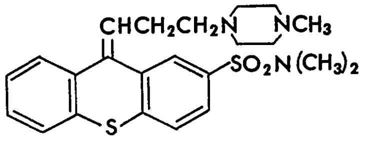
The crystal structure of methixene hydrochloride monohydrate, 9-(*N*-methyl-3-piperidylmethyl)thioxanthene hydrochloride monohydrate, $C_{20}H_{23}NS.HCl.H_2O$, has been determined by the heavy-atom method and refined three-dimensionally by the anisotropic least-squares method to give a final R value of 0·068 for 2228 reflections. The space group is $P2_1/a$ with $Z=4$, and the unit-cell dimensions are $a=15{\cdot}320\pm0{\cdot}003$, $b=9{\cdot}118\pm0{\cdot}002$, $c=13{\cdot}862\pm0{\cdot}004$ Å, and $\beta=94{\cdot}75\pm0{\cdot}02°$. All the hydrogen atoms were located on difference-Fourier syntheses, but their parameters were not refined. The crystal contains both enantiomorphs in an equal amount. The benzenoid rings are normal, and the best planes of the benzene rings make a dihedral angle of 137·9°. The *meso* atoms, C(9) and S, are significantly displaced from the benzene ring. The piperidyl ring is in a chair conformation. The piperidylmethyl group is 'boat axial' with respect to the central thioxanthene ring, and both the thioxanthen-9-ylmethyl and *N*-methyl groups are in an 'equatorial' position with respect to the piperidyl ring. All interatomic distances and angles are normal. The sulfur–carbon bond distance is 1·765 ± 0·003 Å. The average carbon–carbon bond distance is 1·524 ± 0·006 Å for carbon–carbon single bonds, 1·384 ± 0·006 Å for carbon–carbon bonds in the benzenoid ring, and 1·505 ± 0·005 Å for carbon–carbon bonds involving C(9) and the benzenoid ring. The mean value of the nitrogen–carbon bond distance is 1·488 ± 0·006 Å. Each chloride ion is associated with three hydrogen bonds; one links to a quaternary ammonium ion and the other two link to two different water molecules. The packing of the molecules in the crystal is determined by the hydrogen bonding and van der Waals interactions.

Introduction

Methixene (trade name tremaril) is used as an anticholinergic, antispasmodic, or antiparkinsonism drug. This compound is a thioxanthene derivative with the systematic name of 9-(*N*-methyl-3-piperidylmethyl)-thioxanthene (I). Many thioxanthene derivatives possess antipsychotic or anticholinergic activities; however, the correlation of their pharmacological activities with chemical structures has not been established. Thus far, two thioxanthene related antipsychotic agents, thiothixene (II, Schaefer, 1967) and chlorprothixene (III, Dunitz, Eser & Strickler, 1964), have been studied by the single-crystal X-ray diffraction method; however, only two-dimensional analysis has been carried out for chlorprothixene. The crystal structure of a series of drugs derived from the tricyclic ring system has been under study in this laboratory with the objective of correlating the molecular structure with pharmacologiccal activities. The results on methixene hydrochloride are discussed in this paper.



(I)



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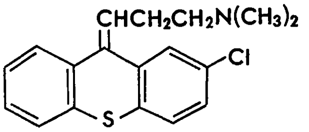

(III)

Crystal data

Methixene hydrochloride was obtained through the courtesy of Dr A. L. Ternay of the Chemistry Department of the University of Texas at Arlington. Transparent, prismatic crystals of this material were grown from a methyl alcohol solution, and the crystals were elongated along the *b* axis. The accurate cell parameters were measured with Mo $K\alpha$ radiation on a Syntex automatic diffractometer. The density of the crystals was determined by the flotation equilibrium method using a mixture of carbon tetrachloride and toluene. These crystals have been found, from the results of structure determination, to be the monohydrate of methixene hydrochloride.

Methixene hydrochloride monohydrate, $C_{20}H_{23}NS.HCl.H_2O$, M.W. 363·95.

Monoclinic, space group $P2_1/a$ from the systematic extinctions:
$h0l$ absent for $h=2n+1$ and $0k0$ absent for $k=2n+1$.

$a=15{\cdot}320\pm0{\cdot}003$ Å $\quad Z=4$
$b=9{\cdot}118\pm0{\cdot}002$ $\quad D_m=1{\cdot}235$ g.cm^{-3}
$c=13{\cdot}862\pm0{\cdot}004$ $\quad D_x=1{\cdot}253$
$\beta=94{\cdot}75\pm\ \pm0{\cdot}02°$ $\quad \mu(\text{Mo } K\alpha)=3{\cdot}11$ cm^{-1}

Experimental

The integrated intensity data were collected on a Datex–Syntex automatic diffractometer. The crystal used was of approximately $0{\cdot}24\times0{\cdot}64\times0{\cdot}21$ mm in dimensions and was mounted along the *b* axis. A $\theta/2\theta$ time variable scanning mode with Mo $K\alpha$ radiation used to measure 3405 independent reflections with 2θ values below 50°, of which 2228 reflections had intensities significantly above the background. The total time for the background counts recorded at the limits of each scan is equal to the scan time. A reflection was considered observed if the intensity was greater than twice of the background. The reference reflections were repeated in intervals of every 100 reflections and they showed fluctuations of 7% intensity over the data collection period. The intensity data were reduced to structure amplitudes using a UNIVAC 1108 program (Shiono, 1971), and no absorption corrections were applied.

Determination and refinement of the structure

The structure was solved by the heavy-atom method. The positions of the chlorine and sulfur atoms were obtained from the Harker sections (u,v,w), $(\frac{1}{2},v,0)$, $(u,\frac{1}{2},w)$, and the vectors between chlorine and sulfur atoms of the sharpened Patterson function. The phases for the first Fourier synthesis were based on the structure-factor calculation (disagreement index, $R=0{\cdot}59$) from the positions of chlorine and sulfur atoms. All carbon and nitrogen atoms were distinctly located in two successive Fourier syntheses. Assuming that the crystal is anhydrous methixene hydrochloride, the structure-factor calculation for all atoms except hydrogen yielded an R value of 0·45 for the three-dimensional data. Two cycles of full-matrix isotropic least-squares refinement reduced the R value to 0·22. Further refinements of one scale factor, the positional and anisotropic thermal parameters for all atoms other than hydrogen were carried out by the full-matrix least-squares UNIVAC 1108 program (Shiono, 1970). Cruickshank's (1961) weighting scheme was used in order to make $[\sum w(F_{\text{calc}}-F_{\text{obs}})^2/(\text{no. of reflections}-\text{no. of parameters})]^{1/2}$ approximately equal to unity. One cycle of anisotropic least-squares refinement reduced R to 0·18, indicating that the structure result was not entirely satisfactory.

The calculation of a difference-Fourier synthesis indicated the presence of one additional atom with an electron density approximately seven times higher than that found at the positions of the remaining peaks representing the hydrogen atoms. Re-examination of the first and second Fourier maps also revealed the presence of an atom with an electron density comparable to that of carbon and nitrogen atoms. Furthermore, the position of this atom is approximately 3 Å from the chloride ion. It is concluded that this atom must be the oxygen atom of a water molecule which is hydrogen bonded to the chloride ion. Since the crystal was crystallized from methyl alcohol, it was not realized earlier that the compound exists as the monohydrate, although the density measurement indicated that probability (the measured density of the crystal was 1·235 g.cm^{-3} as compared with 1·191 and 1·253 g.cm^{-3} respectively for the calculated densities of the anhydrous and hydrated methixene hydrochloride). Two cycles of isotropic least-squares refinement, including the oxygen atom, gave an R value of 0·18, and one cycle of anisotropic least-squares refinement reduced the R value to 0·11. All hydrogen atoms were clearly revealed in the difference Fourier synthesis with reasonable bond lengths and bond angles with respect to the atoms to which they are bonded. Two more cycles of anisotropic least-squares refinement, including all the hydrogen atoms, gave the final R value of 0·068. The positional parameters of the hydrogen atoms were not refined, and they were assigned the same thermal parameters as those of the atoms to which they are bonded. The final positional and thermal parameters are listed in Table 1, and the corresponding structure factors are given in Table 2.

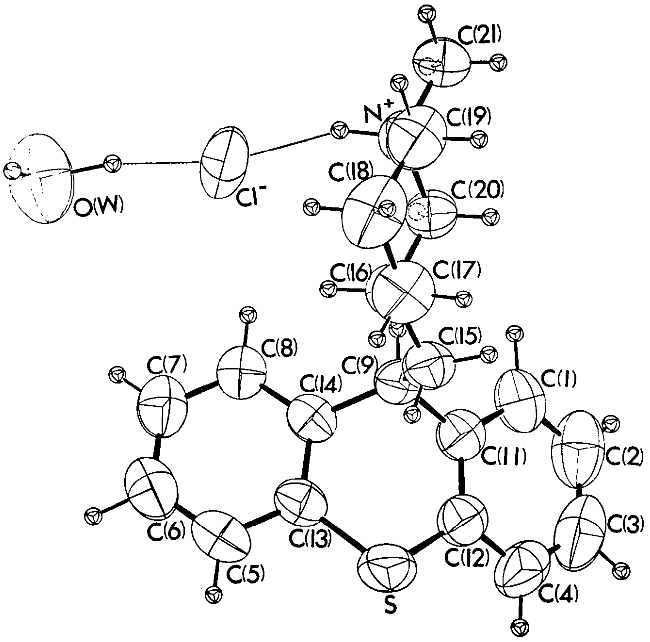

Fig. 1. The structure of one asymmetric unit of methixene hydrochloride monohydrate. Dashed lines are intramolecular hydrogen bonds. The diagram is produced by the *ORTEP* program (Johnson, 1965).
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Table 1. *Fractional atomic coordinates and thermal parameters* (*all* × 10^4)

The estimated standard deviations are given in parentheses and refer to the last decimal positions of respective values. The expression for the temperature factor exponent consistent with β values is:

$$-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\times 10^{-4}.$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	5563 (1)	7242 (1)	280 (1)	90 (1)	161 (2)	93 (1)	43 (1)	−11 (1)	13 (1)
S	3807 (1)	1811 (1)	4625 (1)	56 (1)	238 (2)	52 (1)	11 (1)	8 (0)	15 (1)
N	6622 (2)	4671 (3)	1166 (2)	37 (1)	137 (5)	78 (2)	4 (2)	7 (1)	29 (3)
C(1)	4642 (3)	−611 (5)	2438 (3)	48 (2)	149 (6)	84 (3)	6 (3)	−5 (2)	−23 (4)
C(2)	4557 (3)	−2013 (5)	2776 (4)	59 (3)	131 (7)	132 (5)	0 (3)	−16 (3)	−06 (5)
C(3)	4268 (3)	−2251 (6)	3668 (5)	50 (2)	160 (8)	156 (6)	−1 (4)	−11 (3)	54 (6)
C(4)	4054 (3)	−1077 (6)	4244 (4)	41 (2)	229 (9)	99 (4)	1 (4)	−1 (2)	70 (5)
C(5)	2757 (3)	4023 (5)	3917 (3)	48 (2)	184 (7)	72 (3)	−5 (3)	18 (2)	−18 (4)
C(6)	2413 (3)	4983 (5)	3222 (4)	54 (2)	157 (7)	102 (4)	11 (3)	14 (2)	−11 (4)
C(7)	2735 (3)	4978 (5)	2321 (3)	58 (2)	134 (6)	91 (3)	10 (3)	1 (2)	3 (4)
C(8)	3410 (2)	4052 (4)	2128 (3)	46 (2)	125 (5)	64 (2)	−1 (3)	0 (2)	−2 (3)
C(9)	4550 (2)	2140 (4)	2647 (2)	37 (2)	132 (5)	43 (2)	−3 (2)	1 (1)	0 (3)
C(11)	4431 (2)	600 (4)	2998 (3)	31 (2)	148 (6)	63 (2)	−5 (2)	−3 (2)	9 (3)
C(12)	4128 (2)	337 (5)	3903 (3)	38 (2)	159 (5)	68 (3)	0 (3)	2 (2)	18 (3)
C(13)	3427 (2)	3067 (4)	3720 (3)	38 (2)	150 (6)	58 (2)	−7 (3)	8 (2)	−5 (3)
C(14)	3779 (2)	3103 (4)	2822 (3)	34 (2)	121 (5)	56 (2)	−9 (2)	4 (1)	−11 (3)
C(15)	5410 (2)	2793 (4)	3129 (3)	39 (2)	158 (6)	56 (2)	−5 (3)	2 (2)	8 (3)
C(16)	5782 (2)	4079 (4)	2592 (3)	41 (2)	115 (5)	61 (2)	−5 (2)	−1 (2)	−8 (3)
C(17)	6468 (3)	4919 (5)	3234 (3)	57 (2)	183 (7)	76 (3)	−21 (3)	−12 (2)	−14 (4)
C(18)	6908 (3)	6091 (5)	2659 (4)	63 (3)	151 (7)	113 (4)	−40 (3)	−24 (3)	2 (4)
C(19)	7302 (3)	5457 (5)	1794 (4)	42 (2)	199 (8)	112 (4)	−21 (3)	−6 (2)	35 (5)
C(20)	6189 (2)	3497 (4)	1704 (3)	44 (2)	127 (5)	69 (2)	−8 (3)	10 (2)	13 (3)
C(21)	6992 (3)	4062 (6)	291 (4)	68 (3)	209 (8)	103 (4)	22 (4)	41 (3)	51 (5)
O(W)	3860 (3)	9389 (4)	−172 (3)	78 (2)	233 (7)	179 (4)	−8 (3)	−7 (2)	35 (4)

Table 1 (*cont.*)

Hydrogen atom coordinates (× 10^3)

	x	y	z
H(N)	618	544	93
H(C1)	485	−37	170
H(C2)	461	−281	231
H(C3)	424	−316	399
H(C4)	381	−123	484
H(C5)	249	396	452
H(C6)	185	557	333
H(C7)	249	557	183
H(C8)	366	411	151
H(C9)	463	212	197
H(C15)1	587	204	313
H(C15)2	527	313	377
H(C16)	529	477	237
H(C17)1	692	423	349
H(C17)2	620	528	377
H(C18)1	646	686	244
H(C18)2	739	658	303
H(C19)1	757	615	136
H(C19)2	777	472	198
H(C20)1	662	278	190
H(C20)2	570	306	121
H(C21)1	652	355	−3
H(C21)2	739	335	43
H(C21)3	731	480	0
H(O*W*)1	454	872	6
H(O*W*)2	409	1045	−9

Description of the structure

The configuration of a methixene hydrochloride monohydrate molecule and the identification of the atoms are shown in Fig. 1. Since the crystal belongs to a centrosymmetric space group, both enantiomorphs are present in the crystal.

The bond lengths and bond angles with their standard deviations are shown in Table 3. The C–C bond lengths within the benzene rings range from 1·364 to 1·403 Å with a mean value of 1·384 Å which is in good agreement with 1·385 Å for *cis*-9-methylthioxanthene 10-oxide (Jackobs & Sundaralingam, 1969) and 1·38 Å for *trans*-thioxanthen-9-ol 10-oxide (Ternay, Chasar & Sax, 1967). The C–C bond lengths involving C(9) of the central ring are 1·502 and 1·508 Å which are in agreement with the normal Csp^3–Csp^2 bond distance of 1·50 Å. The C–C bond lengths in the piperidyl ring and that between ring and exocyclic carbons range from 1·502 to 1·546 Å, and none of these differs significantly from the mean value of 1·524 Å.

The mean value of the two carbon–sulfur bond lengths is 1·765 Å which is in agreement with the Csp^2–S bond with a coordination number of two for the sulfur atom, *e.g.* 1·771 Å in thianthrene (Rowe & Post, 1958), and 1·77 Å in phenothiazine (Bell, Blount, Briscoe & Freeman, 1968). The mean value of the three carbon–nitrogen bond lengths is 1·488 Å which is in agreement with the Csp^3–Nsp^3 bond length of 1·47 Å (Pauling, 1960).

The valence angles in the benzenoid rings are normal. The least-squares planes in methixene are shown in Table 4. The central ring is in a boat conformation, and the displacements of C(9) and S are on the opposite sides of the benzene planes which has also been found in *cis*-9-methylthioxanthene 10-oxide (Jackobs & Sundaralingam, 1969). The dihedral angle between the least-squares planes of the two benzene rings is 137·9°, which is slightly smaller than that of 141·5° in thiothixene (Schaefer, 1967). The piperidyl methyl group is 'boat-axial' with respect to the central thioxanthene ring. This result is in agreement with the conformation of methixene hydrochloride in solutions deduced from nuclear magnetic resonance studies (Ternay, 1972). The thioxanthen-9-ylmethyl group is equatorial with respect to the piperidyl ring. The six-membered ring of the piperidyl group is in a chair con-

Table 2 *Observed and calculated structure factors*

Columns are: index, $|F_{\text{obs}}|$, F_{cal}
* For unobserved reflections.

[illegible]

Table 2 (*cont.*)

formation, and the *N*-methyl group is in a equatorial position. The conformation angles of the piperidyl ring are given in Table 5, and the torsion angles about the C(9)–C(15), C(15)–C(16), and N–C(19) bonds are shown in Fig. 2. (The conformation and torsion angles were calculated from the coordinates for the enantiomorph given in Table 1. The enantiomeric structure will have the conformation and torsion angles of the same magnitude but of opposite sign.)

There are two hydrogen bonds within one molecular unit of methixene hydrochloride monohydrate. One is formed between the quaternary ammonium ion and chloride ion, and the other one links the water molecule with the chloride ion. The packing of the molecules in the crystal is illustrated in Fig. 3. Each chloride ion is associated with three hydrogen bonds, and each water molecule has two hydrogen bonds. The hydrogen-bond distances and angles are shown in Table 6. The non-bonded distances which are less than 3·5 Å are also listed in Table 6. All structural interpretation

Table 3. *Bond lengths and bond angles* (*with estimated standard deviations in parentheses*)

S——C(12)	1·769 (3) Å	C(12)–S——C(13)	100·5 (2)°
S——C(13)	1·761 (3)	C(19)–N——C(20)	111·9 (3)
N——C(19)	1·485 (6)	C(19)–N——C(21)	111·2 (3)
N——C(20)	1·492 (5)	C(20)–N——C(21)	110·8 (3)
N——C(21)	1·487 (6)	C(2)—C(1)—C(11)	120·8 (4)
C(1)—C(2)	1·371 (7)	C(1)—C(2)—C(3)	120·4 (5)
C(1)—C(11)	1·403 (6)	C(2)—C(3)—C(4)	120·5 (5)
C(2)—C(3)	1·364 (8)	C(3)—C(4)—C(12)	119·5 (4)
C(3)—C(4)	1·391 (7)	C(6)—C(5)—C(13)	120·5 (4)
C(4)—C(12)	1·381 (6)	C(5)—C(6)—C(7)	119·2 (4)
C(5)—C(6)	1·374 (6)	C(6)—C(7)—C(8)	120·5 (4)
C(5)—C(13)	1·391 (6)	C(7)—C(8)—C(14)	121·3 (4)
C(6)—C(7)	1·380 (6)	C(11)–C(9)—C(14)	112·0 (3)
C(7)—C(8)	1·378 (6)	C(11)–C(9)—C(15)	110·0 (3)
C(8)—C(14)	1·380 (5)	C(14)–C(9)—C(15)	110·9 (3)
C(9)—C(11)	1·502 (5)	C(1)—C(11)–C(9)	121·1 (3)
C(9)—C(14)	1·508 (5)	C(1)—C(11)–C(12)	118·2 (3)
C(9)—C(15)	1·546 (5)	C(9)—C(11)–C(12)	120·7 (3)
C(11)–C(12)	1·393 (5)	S——C(12)–C(4)	118·8 (3)
C(13)–C(14)	1·397 (5)	S——C(12)–C(11)	120·5 (3)
C(15)–C(16)	1·524 (5)	C(4)—C(12)–C(11)	120·8 (4)
C(16)–C(17)	1·526 (6)	S——C(13)–C(5)	118·3 (3)
C(16)–C(20)	1·521 (5)	S——C(13)–C(14)	121·4 (3)
C(17)–C(18)	1·523 (7)	C(5)—C(13)–C(14)	120·4 (4)
C(18)–C(19)	1·502 (7)	C(8)—C(14)–C(9)	122·3 (3)
		C(8)—C(14)–C(13)	118·0 (3)
		C(9)—C(14)–C(13)	119·7 (3)
		C(9)—C(15)–C(16)	115·1 (3)
		C(15)–C(16)–C(17)	111·6 (3)
		C(15)–C(16)–C(20)	108·8 (3)
		C(17)–C(16)–C(20)	109·3 (3)
		C(16)–C(17)–C(18)	111·1 (4)
		C(17)–C(18)–C(19)	111·9 (4)
		N——C(19)–C(18)	110·2 (4)
		N——C(20)–C(16)	112·5 (3)

Table 5. *Conformation angles**

Within the piperidyl ring

C(16) → C(17)	+52·9°
C(17) → C(18)	−55·5
C(18) → C(19)	+56·6
C(19) → N	−56·8
N → C(20)	+56·7
C(20) → C(16)	−53·9

* The conformation angle of a directed bond C(17) → C(18) is defined as the angle that the projection of the bond C(16) → C(17) makes with respect to the projection of the bond C(17) → C(18). The angle is positive if it is measured clockwise (Klyne & Prelog, 1960).

Table 6. *Hydrogen-bond distances and angles*

i	*j*	*k*	*D*(*ij*)	*D*(*jk*)	∠*ijk*
N	Cl	O	3·051 Å	3·280 Å	157·5°
N	Cl	O(*a*)*	3·051	3·203	128·0
O	Cl	O(*a*)	3·280	3·203	68·7
Cl	N	C(19)	3·051		100·9
Cl	N	C(20)	3·051		120·6
Cl	N	C(21)	3·051		100·6
Cl	O	Cl(*a*)	3·280	3·203	116·6

Intermolecular non-bonded distancess less than 3·5 Å

i	*j*	*D*(*ij*)
O	C(20) (*b*)	3·378 Å
O	C(21) (*c*)	3·302
O	C(21) (*b*)	3·406

* Symmetry code

None	x	y	z
(*a*)	$1-x$	$2-y$	$-z$
(*b*)	$1-x$	$1-y$	$-z$
(*c*)	$-\frac{1}{2}+x$	$\frac{3}{2}-y$	z

Table 4. *Least-squares planes in methixene and the displacements of atoms from the plane*

Equation of planes: $Ax+By+Cz=D$, where x, y, z are in Å.

Plane	*A*	*B*	*C*	*D*
(*a*)	0·9107	0·0337	0·3350	7·5886
(*b*)	0·9027	0·0332	0·3528	7·6178
(*c*)	0·6430	0·6942	0·2691	6·7213
(*d*)	0·6295	0·6937	0·2966	6·7719
(*e*)	0·8104	0·3905	0·3682	7·2408

Displacements in Å from the least-squares planes

Benzene ring					
Atom	(*a*)	(*b*)	Atom	(*c*)	(*d*)
C(1)	0·001	−0·024	C(5)	0·003	0·043
C(2)	−0·003	−0·019	C(6)	0·011	0·032
C(3)	0·000	0·010	C(7)	−0·011	−0·032
C(4)	0·005	0·032	C(8)	−0·004	−0·045
C(11)	0·004	−0·005	C(13)	−0·017	0·002
C(12)	−0·007	0·009	C(14)	0·017	−0·005
S	−0·074*	−0·036	S	−0·099*	−0·053
C(9)	0·054*	0·033	C(9)	0·102*	0·058

Central ring	
Atom	(*e*)
C(11)	0·005
C(12)	−0·004
C(13)	0·004
C(14)	−0·005
S	0·491*
C(9)	0·521*

* Indicates atoms excluded from the calculation of the least-squares planes.

Dihedral angles between the last squares planes

Planes	Dihedral angle
(*a*) and (*c*)	137·9°
(*b*) and (*d*)	137·9
(*a*) and (*b*)	1·1
(*c*) and (*d*)	1·7

data reported here were calculated on the UNIVAC 1108 computer (Chu, 1971).

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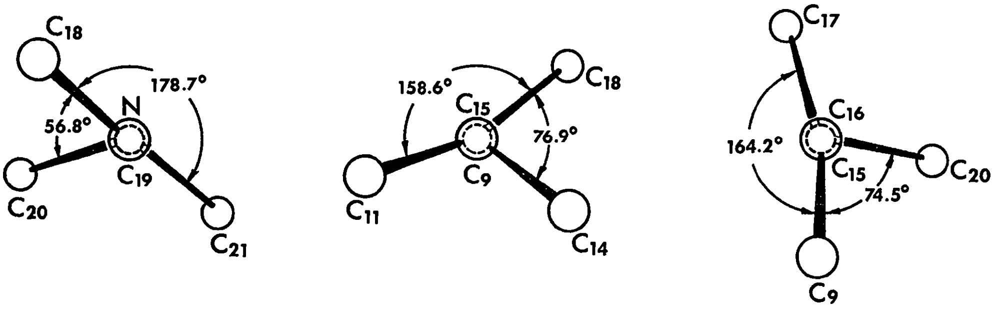

(*a*) (*b*) (*c*)

Fig. 2. The torsion angles about the (*a*) C(19)–N, (*b*) C(9)–C(15), and (*c*) C(15)–C(16) bonds.

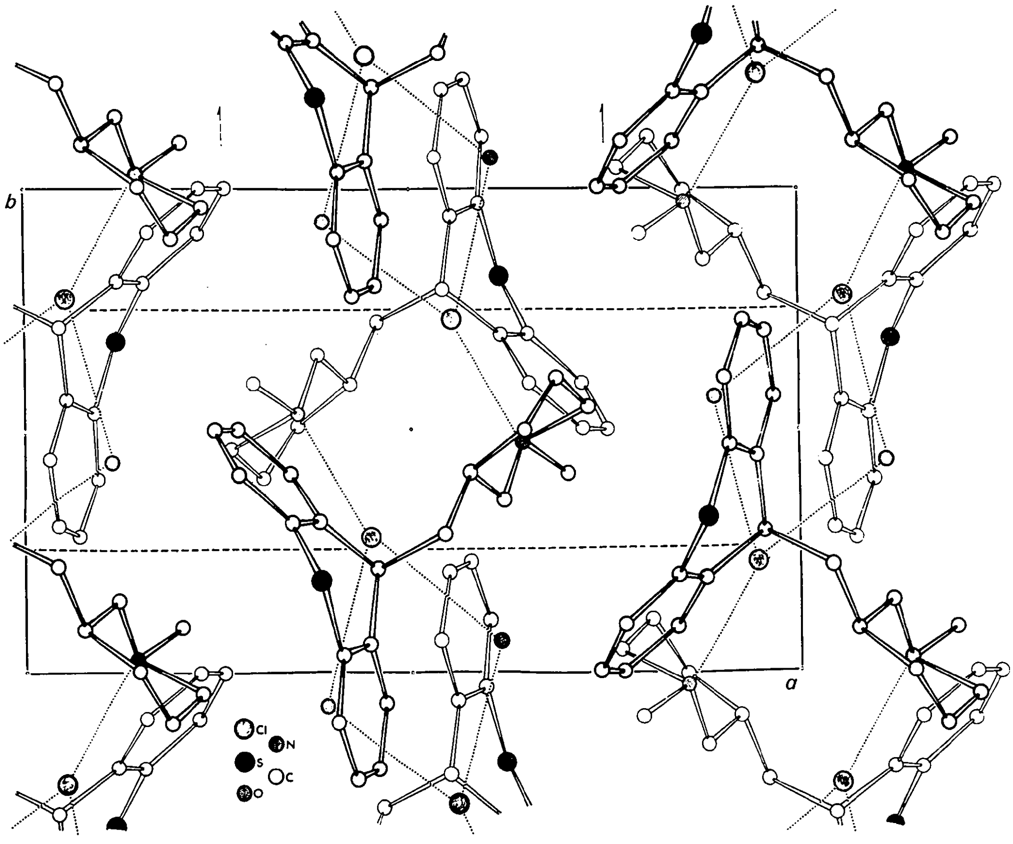

Fig. 3. The molecular packing and hydrogen bonding in methixene hydrochloride monohydrate. The dashed lines are hydrogen bonds.

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The Crystal Structure of 1,4-Bis(diazo)-2,3-butanedione

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1,4-Bis(diazo)-2,3-butanedione, $C_4H_2N_4O_2$, crystallizes in the monoclinic space group $P2_1/n$, $a=3{\cdot}745$ (1), $b=8{\cdot}326$ (2), $c=9{\cdot}580$ (2) Å, $\beta=93{\cdot}12$ (1)° with two molecules in the unit cell. The structure was determined from 614 reflections (Cu $K\alpha$, $2\theta_{\max}=160°$, Picker diffractometer) and refined to $R=0{\cdot}029$. The molecules are planar, with the CO.CH.N_2 moiety in the *cis* configuration. Distances (e.s.d. 0·001–2 Å): C–O, 1·222; C–C(H), 1·418; C–N, 1·313; N–N, 1·114; central C–C 1·531 Å. Angles: O–C–C(H), 125·2; C–C–N, 116·5; C–N–N, 176·8 (toward C=O group); C–C–C, 114·0°. No evidence for hydrogen bonding could be found.

Introduction

In recent years α-diazoketones have come into use as important reaction intermediates, and as a result their physical-chemical properties have been studied by several authors. Fahr (1960) undertook spectroscopic studies of a group of α-diazoketones with the general formula N_2.CH.CO.$(CH_2)_n$.CO.CH.N_2. He tacitly assumed the *cis* configuration for the N_2.CH.CO moiety. Kaplan & Meloy (1966), on the other hand, studied the *cis–trans* equilibrium for some α-diazoketones. They found that the majority configuration was *cis*, but the admixture of *trans* was not insignificant. The configuration has also been the object of a theoretical study by Csizmadia, Houlden, Meresz & Yates (1969). Their results are in general agreement with those of Kaplan & Meloy.

The simplest of the compounds studied by Fahr (1960) is 1,4-bis(diazo)-2,3-butanedione (DBD), corresponding to $n=0$ in the formula given above. It is an easily crystallized compound which melts reversibly at 125 °C, and it was therefore considered suitable for an X-ray study, which was prompted by the apparent lack of structural data for this class of compounds. The results of this study are reported here.

Experimental

The crystals, grown from methanol solution, are yellow needles elongated along **a**. A specimen of dimensions 0·12 × 0·12 × 0·30 mm, cut from a longer needle, was used for the diffraction measurements. Because DBD is quite volatile we sealed the crystal in a thin-walled glass capillary.

From oscillation and Weissenberg photographs monoclinic symmetry as well as the space-group extinctions $h0l$ for $h+l$ odd and $0k0$ for k odd were established. The space group therefore is $P2_1/n$.

Cell dimensions were obtained by a least-squares fit to eight 2θ, φ, χ sets measured on a Picker diffractometer. They are $a=3{\cdot}745$ (1), $b=8{\cdot}326$ (2), $c=9{\cdot}580$ (2) Å, $\beta=93{\cdot}12°$ (1). (λCu $K\alpha_1=1{\cdot}54051$ Å, $t=24$ °C). The density observed by flotation/pycnometry is 1·537 g.cm^{-3} and that calculated for $Z=2$ is 1·536 g.cm^{-3}.

Intensity data up to $2\theta=160°$ were measured automatically by the θ–2θ scan method, using Ni-filtered Cu $K\alpha$ radiation. Because we did not trust the stability of the crystal an initial data set was collected in 24 hr (2θ scan speed 2° min^{-1}). As no sign of deterioration could be detected a second data set was collected at a scan speed of 1° min^{-1}; these data also gave no evidence of deterioration.

The intensities were corrected for background (measured at the extremes of each scan) and Lorentz and polarization effects. No absorption correction was applied. Standard deviations, $\sigma(N)$, were assigned to each recorded number of counts, N, by $\sigma(N)=[N+(0{\cdot}005N)^2]^{1/2}$. The factor 0·005 approximately reproduces the observed variance in the check reflections which were monitored every 50 reflections.

The two data sets were merged, with weights according to the assigned $\sigma(F)$ values. All 614 measured reflections were treated as 'observed'.

Determination of the structure

DBD is required to posses a center of symmetry, so that the asymmetric unit contains half a molecule. The