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Structure of 3-Dimethylamino-2-(2-formyl-3,4-dihydro-1-naphthyl)-*N*,*N*-dimethyl-2-propeniminium Chloride Dihydrate: A Vilsmeier Intermediate

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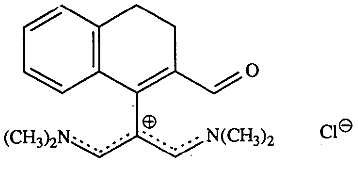
Abstract. $[C_{18}H_{23}N_2O]^+.Cl^-.2H_2O$, $M_r = 354{\cdot}878$, monoclinic, $P2_1$, $a = 9{\cdot}0806\,(23)$, $b = 7{\cdot}5717\,(15)$, $c = 14{\cdot}4414\,(51)$ Å, $\beta = 106{\cdot}922\,(24)^\circ$, $V = 949{\cdot}94\,(46)$ Å^3, $Z = 2$, $D_x = 1{\cdot}241$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 19{\cdot}3$ cm^{-1}, $F(000) = 380$, $T = 300$ K, $R = 0{\cdot}046$, $wR = 0{\cdot}045$ for 1261 reflections with $F_o \geq 2\sigma(F_o)$. The unit cell consists of the two cations and two anions linked by hydrogen bonds involving the four water molecules. The remarkable stability of the trisubstituted allyl cation is due to delocalization of the positive charge along the chain.

Introduction. Vilsmeier reagents (Mundy & Ellerd, 1988) are important synthetic tools in organic chemistry. As part of a continuing study of Vilsmeier reagents, the reaction of $POCl_3/(CH_3)NCHO$ with 3,4-dihydro-1-methylnaphthalene was reported by Katritzky & Marson (1987). In addition to the final product 1-[2-(*N*,*N*-dimethylamine)-1-formylvinylene]-3,4-dihydronaphthalene-2-carboxaldehyde (I), another product was obtained on several occasions. This product differed in the melting point but appeared to be very similar to (I). Therefore, an X-ray study was undertaken to determine the nature of this apparent intermediate in the reaction.



Experimental. The title compound forms canary-yellow crystals from ethyl acetate. Upon heating, the crystals appear to lose solvent at about 363 K followed by a color change. At 413 K there still appeared to be unmelted material. In contrast the final product (I) has a melting point 406–407 K.

Intensity data were collected with nickel-filtered Cu $K\alpha$ radiation using a $P\bar{1}$ diffractometer upgraded to a Nicolet $P3$. The crystal had dimensions $0{\cdot}03 \times 0{\cdot}17 \times 0{\cdot}25$ mm and was mounted on a glass fiber. The cell constants and orientation matrix were determined from 24 reflections in the 2θ range $10{\cdot}0$–$31{\cdot}5^\circ$. The intensity data were measured using a variable speed ($1{\cdot}9$–$29{\cdot}3^\circ$ min^{-1}) θ–2θ scan. The 2θ range was $1{\cdot}5$–$112{\cdot}5^\circ$ ($-9 \leq h \leq 9$, $0 \leq k \leq 8$, $0 \leq l \leq 15$). Two standard reflections were measured after every 98 reflections and showed a slow decrease of about 5% [$6\sigma(I)$] over the time of data collection. The standards were used to derive a correction for the data. A total of 1495 measurements was reduced to 1366 unique reflections. The 1261 reflections with $F_{\rm obs} \geq 2\sigma(F_{\rm obs})$ were used in the analysis.

The structure was solved by direct methods and refined on F by blocked-cascade least-squares methods. The refinement of the chiralty parameter, η, defined by Rogers (1981) was used to establish the absolute configuration given in Fig. 1. A difference Fourier synthesis was used to locate the 27 H atoms. The H-atom positions in the four methyl groups were idealized to a tetrahedral arrangement. The other H-atom positions were those found in the difference Fourier synthesis. An isotropic U of $0{\cdot}05$ Å^2 was used for all the H atoms. The H-atom parameters were not refined. An extinction correc-

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Table 1. *Atomic coordinates and isotropic thermal parameters* (Å^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cl	0·1431 (2)	0·6711 (3)	0·4480 (1)	0·067 (1)
N(1)	0·3760 (4)	0·2701 (5)	0·4334 (2)	0·040 (1)
N(2)	−0·1288 (4)	0·0364 (6)	0·2648 (3)	0·048 (1)
O(1)	−0·0643 (4)	0·5794 (6)	0·1445 (2)	0·076 (2)
O*W*(1)	0·1759 (4)	−0·0220 (6)	0·5995 (3)	0·078 (2)
O*W*(2)	0·6494 (5)	0·4471 (8)	0·2049 (4)	0·113 (2)
C(1)	0·1607 (4)	0·1956	0·2228 (3)	0·038 (1)
C(2)	0·1056 (5)	0·3388 (6)	0·1676 (3)	0·041 (2)
C(3)	0·1234 (5)	0·3567 (7)	0·0677 (3)	0·051 (2)
C(4)	0·2763 (6)	0·2739 (7)	0·0641 (3)	0·053 (2)
C(5)	0·2955 (5)	0·0927 (7)	0·1062 (3)	0·043 (2)
C(6)	0·3679 (6)	−0·0407 (8)	0·0704 (3)	0·058 (2)
C(7)	0·3893 (6)	−0·2062 (7)	0·1126 (4)	0·062 (2)
C(8)	0·3368 (6)	−0·2396 (7)	0·1911 (4)	0·057 (2)
C(9)	0·2645 (5)	−0·1116 (7)	0·2287 (3)	0·046 (2)
C(10)	0·2424 (5)	0·0569 (6)	0·1868 (3)	0·038 (1)
C(11)	0·0116 (6)	0·4704 (7)	0·1986 (3)	0·053 (2)
C(12)	0·1312 (4)	0·1688 (7)	0·3190 (3)	0·035 (1)
C(13)	0·2351 (5)	0·2067 (6)	0·4079 (3)	0·040 (2)
C(14)	0·4540 (5)	0·3089 (8)	0·5347 (3)	0·055 (2)
C(15)	0·4603 (6)	0·3235 (8)	0·3660 (4)	0·063 (2)
C(16)	−0·0057 (5)	0·0965 (6)	0·3294 (3)	0·042 (2)
C(17)	−0·1566 (6)	0·0225 (8)	0·1614 (3)	0·066 (2)
C(18)	−0·2580 (7)	−0·0306 (11)	0·2988 (5)	0·093 (3)

tion of the form $F_c = F_c/(1 + gF_c^2/\sin 2\theta)^{1/4}$ was used in the refinement. The final R was 0·044 and $wR = [\sum(w\Delta F^2)/\sum wF_o^2]^{1/2}$ was 0·045 with a GOF of 1·59 and $g = 2{\cdot}5 \times 10^{-5}$. The weights were $w = [\sigma^2(F) + 0{\cdot}0005F^2]^{-1}$. The ratio of the max. shift/e.s.d. was 0·09 in the last least-squares cycle. The final difference Fourier synthesis was featureless with a maximum density of +0·17 e Å^{-3} and a minimum of −0·19 e Å^{-3}. The scattering factors used were those in the *SHELXTL* package and are in the analytical form given in *International Tables for X-ray Crystallography* (1974). All calculations were performed using the *SHELXTL* package (Sheldrick, 1986). The final positional parameters are given in Table 1, with bond lengths, bond angles and torsion angles in Table 2.* A view of the cation is given in Fig. 1.

Discussion. The unit cell consists of two cations, two anions and four water molecules in a hydrogen-bonded network. The water molecule O*W*(1) forms two hydrogen bonds to two different Cl$^-$ ions related by the 2_1 axis at distances of 3·137 and 3·145 Å. The result is an infinite chain of Cl$^-$ and H_2O molecules. The second water molecule O*W*(2) hydrogen bonds to both the cation *via* O(1) at 3·138 Å and water molecule O*W*(1) at 2·817 Å. The distances are normal for O···Cl and O···O hydrogen bonds.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°)

C(1)—C(2)	1·353 (5)	C(1)—C(10)	1·466 (6)
C(1)—C(12)	1·503 (6)	C(2)—C(3)	1·503 (6)
C(2)—C(11)	1·465 (7)	C(3)—C(4)	1·538 (7)
C(4)—C(5)	1·489 (7)	C(5)—C(6)	1·385 (8)
C(5)—C(10)	1·410 (7)	C(6)—C(7)	1·382 (8)
C(7)—C(8)	1·375 (9)	C(8)—C(9)	1·369 (8)
C(9)—C(10)	1·401 (7)	C(11)—O(1)	1·206 (6)
C(12)—C(13)	1·384 (5)	C(12)—C(16)	1·406 (6)
C(13)—N(1)	1·315 (6)	N(1)—C(14)	1·457 (5)
N(1)—C(15)	1·460 (7)	C(16)—N(2)	1·311 (5)
N(2)—C(17)	1·444 (6)	N(2)—C(18)	1·488 (9)
C(2)—C(1)—C(10)	120·2 (4)	C(2)—C(1)—C(12)	121·2 (4)
C(10)—C(1)—C(12)	118·5 (3)	C(1)—C(2)—C(3)	120·9 (4)
C(1)—C(2)—C(11)	120·8 (4)	C(3)—C(2)—C(11)	117·9 (4)
C(2)—C(3)—C(4)	110·2 (3)	C(3)—C(4)—C(5)	111·2 (4)
C(4)—C(5)—C(6)	122·1 (5)	C(4)—C(5)—C(10)	119·1 (4)
C(6)—C(5)—C(10)	118·8 (5)	C(5)—C(6)—C(7)	121·2 (5)
C(6)—C(7)—C(8)	119·5 (5)	C(7)—C(8)—C(9)	121·2 (5)
C(8)—C(9)—C(10)	119·9 (5)	C(1)—C(10)—C(5)	119·0 (4)
C(1)—C(10)—C(9)	121·5 (4)	C(5)—C(10)—C(9)	119·4 (4)
C(2)—C(11)—O(1)	122·8 (5)	C(1)—C(12)—C(13)	124·9 (4)
C(1)—C(12)—C(16)	123·5 (3)	C(13)—C(12)—C(16)	111·5 (4)
C(12)—C(13)—N(1)	132·9 (4)	C(13)—N(1)—C(14)	120·3 (4)
C(13)—N(1)—C(15)	124·8 (3)	C(14)—N(1)—C(15)	114·7 (4)
C(12)—C(16)—N(2)	131·0 (4)	C(16)—N(2)—C(17)	128·2 (4)
C(16)—N(2)—C(18)	118·3 (4)	C(17)—N(2)—C(18)	113·5 (4)
C(1)—C(2)—C(3)—C(4)	−34·1 (6)	C(2)—C(1)—C(12)—C(13)	−99·8 (5)
C(2)—C(3)—C(4)—C(5)	49·6 (5)	C(2)—C(1)—C(12)—C(16)	82·1 (5)
C(3)—C(4)—C(5)—C(10)	−36·6 (5)	C(10)—C(1)—C(12)—C(13)	84·1 (5)
C(4)—C(5)—C(10)—C(1)	4·0 (5)	C(10)—C(1)—C(12)—C(16)	−94·0 (5)
C(5)—C(10)—C(1)—C(2)	15·3 (5)	C(1)—C(12)—C(13)—N(1)	−0·2 (8)
C(10)—C(1)—C(2)—C(3)	1·5 (6)	C(1)—C(12)—C(16)—N(2)	1·6 (8)

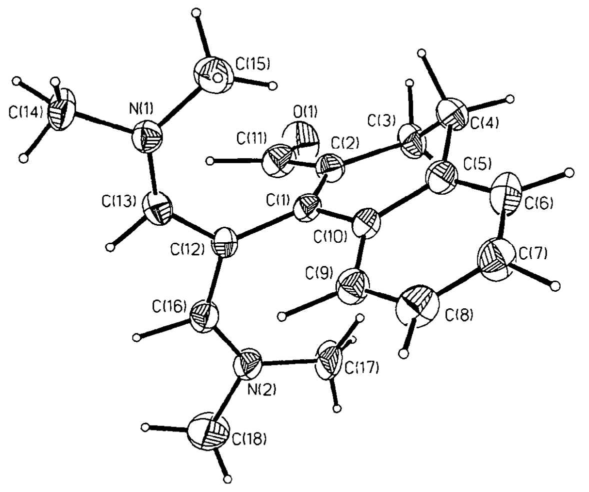

Fig. 1. A view of the 3-dimethylamino-2-(2-formyl-3,4-dihydro-1-naphthyl)-*N*,*N*-dimethyl-2-propeniminium cation showing the atomic numbering scheme and thermal ellipsoids.

The cation can be conveniently viewed as a dihydronaphthalene group bonded to the delocalized, formally positively charged allyl side chain. Since the torsion angles about the C(1)—C(12) bond are approximately 90° (see Table 2), no interactions

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52670 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

exist between the two groups. In the 2-formyl-3,4-dihydronaphthalene group, the six-membered aromatic ring C(5)—C(10) is planar within experimental error, but the ring formed by C(1) to C(5) and C(10) is not. The torsion angles in Table 2 suggest an approximate twofold axis bisecting the C(3)—C(4) and C(1)—C(10) bonds. Therefore, the ring is best described as a 1,3-diplanar form or twist-chair-boat conformation. The formyl group is twisted by 20·8° from the C(1)—C(2)—C(5)—C(10) plane.

This report is the first confirmation by X-ray diffraction of the intermediate proposed by Meth-Cohn & Taljaard (1983) and Meth-Cohn (1987). The side chain is particularly interesting since this is the site of the positive charge. The delocalization of the positive charge in the side chain accounts for the stability of the allyl cation which allows this intermediate to be isolated from an aqueous solution. The C(1)—C(12) bond of 1·501 (6) Å is typical of a $C(sp^2)$—$C(sp^2)$ single bond which is in agreement with the assumption of no interaction between the ring and side chain. The side chain atoms N(1)—C(13)—C(12)—C(16)—N(2) are planar and coplanar. However, there are significant deviations of the angles from 120° which appear to be related to steric interactions. All the angles which face the dihydronaphthalene group are larger than 120° (the range is 123·2 to 132·9°), reducing steric interactions.

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Structure of 2,3-Dihydro-5-nitro-6-phenyl-1,4-dithiin

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Abstract. $C_{10}H_9NO_2S_2$, $M_r = 239·3$, monoclinic, $P2_1/c$, $a = 5·822$ (1), $b = 15·367$ (3), $c = 12·137$ (2) Å, $\beta = 103·5$ (2)°, $V = 1056·0$ (6) Å^3, $Z = 4$, $D_x = 1·51$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 4·6$ cm^{-1}, $F(000) = 496$, $T = 294$ K, $R = 0·0408$ for 1764 observed reflections. Because one C atom is disordered over two sites, the six-membered dithiin ring adopts two different conformations in the crystal structure, one a twisted half boat and the other a cyclohexene half chair. The nitro- and phenyl-group planes are inclined at 22·2 and 68·5° respectively to the plane of the S—C=C—S moiety.

Introduction. 2,3-Dihydro-1,4-dithiin tetroxides are a class of compounds with varied and powerful biological activities. Depending on the type and positions of substitution, members of this class may have strong herbicidal (Brewer, Neidermeyer & McIntyre, 1975), plant growth regulant (Brewer, Neidermeyer & McIntyre, 1976; McIntyre, Lambert & Brewer, 1977), fungicidal (Brewer & Davis, 1977), or viricidal (Brewer & Davis, 1978) activity. Two crystallographic studies of dihydrodithiin tetroxides have been published previously (Arora, Bates, Kriek & Brewer, 1978; Bates, Kriek & Brewer, 1980).

By contrast, the unoxidized dihydrodithiins are essentially devoid of biological activity (Brewer, 1985). Very few simple 1,4-dithiins have been studied by X-ray methods (Howell, Curtis & Lipscomb, 1954; Kobayashi & Iwasaki, 1984) and the most simple compounds in this area are liquids at room temperature. We now report the results of our X-ray

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