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Synthesis and Crystal Structure of 4,4′(1,2-Ethanediyldiimino)bis(1,1,1-trichloro-3-penten-2-one)

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The preparation, characterization and crystal structure of the *Schiff* base obtained from 1,1,1-trichloroacetylacetone and ethylenediamine is reported. The structural determination shows that the compound is 4,4′(1,1-ethanediyldiimino)bis(1,1,1-trichloro-3-penten-2-one), it suggests that the electron accepting ability of the CCl_3 group induces a larger $\delta +$ charge on the remote carbonyl. In the solid state it occurs in two different conformations and N—H---O hydrogen bond is present.

(Keywords: Electron accepting ability of —CCl_3; *Schiff base)*

Synthese und Kristallstruktur von 4,4′(1,2-Ethandiyldiimino)bis(1,1,1-Trichlor-3-penten-2-on)

Es wird über die Darstellung, Charakterisierung und Kristallstruktur der *Schiff*-Base berichtet, die aus 1,1,1-Trichloracetylaceton und Ethylendiamin erhalten wurde. Die Röntgenstrukturanalyse zeigte, daß es sich um 4,4′(1,1-Ethandiyldiimino)bis(1,1,1-trichlor-3-penten-2-on) handelt. Dies impliziert, daß die Elektronacceptorfähigkeit der CCl_3-Gruppe eine größere Partialladung $\delta +$ im entfernteren Carbonyl induziert. Die Verbindung besitzt im Kristall zwei verschiedene Konformationen. Es wurde eine N—H----O-Wasserstoffbrückenbindung festgestellt.

Introduction

The reaction between 1,1,1-trifluoroacetylacetone and ethylenediamine leads to the corresponding *Schiff* base (*TFAEN*) whose structure arises from the nucleophilic attack on the remote carbonyl to the CF_3 group[1]. In this paper we report the synthesis, spectroscopic characterization and crystal structure of the chlorinated homologous compound 4,4′(1,2-ethanediyldiimino)bis(1,1,1-trichloro-3-penten-2-one) (*TCAEN*) in order to know if the electron-accepting ability of the CCl_3 group induces a larger $\delta +$ charge on the remote carbonyl or in the carbonyl linked to the CCl_3 in the 1,1,1-trichloroacetylacetone.

Experimental

The melting point (m.p.) was determined with an Osyma apparatus and is uncorrected. Elemental analysis was determined in a commercial laboratory. The infrared absorption spectra were taken by a Perkin-Elmer 283 spectrophotometer. The proton magnetic resonance spectra were obtained on a Varian FT-80 spectrometer (*TMS* as internal standard). Mass spectra were determined with a Hewlett-Packard 5985-B spectrometer.

TCAEN was prepared and purified from 1,1,1-trichloroacetylacetone[2,3] and ethylenediamine by a similar method as described for the synthesis of *TFAEN*[4].

Single crystals of *TCAEN* were grown by slow evaporation from acetone solution. These crystals are shining, transparent and fairly large prismatic and proved to be suitable for the X-ray analysis. Crystals of *TCAEN*, $M = 430.9$, are monoclinic, space group $P\,2_{1/c}$ with unit cell constants: $a = 15.915\,(3)$, $b = 8.867\,(1)$, $c = 12.517\,(3)\,Å$, $\beta = 94.92\,(4)°$, $U = 1\,759.9\,Å^3$, $F(000) = 872$, $\mu\,(\mathrm{Cu\,K_\alpha}) = 92.07\,\mathrm{cm^{-1}}$, $T = 293°\,\mathrm{K}$, $\rho_{\mathrm{obsd}} = 1.65$, $\rho_{\mathrm{cald}} = 1.62\,\mathrm{g\,cm^{-3}}$ for $z = 4$.

Intensities from a crystal, 0.24 × 0.30 × 0.38 mm, were collected on a Nicolet R 3 m automated diffractometer using graphite monochromatized $\mathrm{Cu\,K_\alpha}$ radiation ($\lambda = 1.5418\,Å$) and the unit-cell dimensions determined from the setting angles of 15 machine-centred reflections. Data collection (θ–2θ scans, background-peak-background, $3 < 2\theta < 116°$) yielded 2681 measured reflections with $I > 2.5\,\sigma\,(I)$. The intensities were corrected for the *Lorentz* polarization factor but an absorption was not applied. The crystal structure was solved by direct methods using the program package SHELXTL[5]. The program SOLV was employed using 170 phases with $|E| > 1.20$ and 10 reflections in the starting set. The trial structure was refined by a blocked cascade least-squares procedure with anisotropic temperature factors for the non-H atoms and with a fixed isotropic temperature factor, $U = 0.06\,Å^2$ for the H atoms bonded to C atoms; and the coordinates of the H atoms of the N(1)-H and N(2)-H were refined. The function minimized was $\sum \omega\,|\Delta F|^2$ with a weighting scheme $\omega^{-1} = |\sigma^2(F_0) + G(F_0)^2|$ with a final $G = 0.00076$; no peaks $> 0.3\,\mathrm{e}\,Å^{-3}$; atomic scattering factors from International Tables for X-ray Crystallography[6]. Final weighted $R = 0.054$ (unweighted $R = 0.061$). All computations were performed in a Nova 4 computer and plots were drawn on a Tektronix plotter. The final atomic coordinates and U_{eq} values are presented in Table 1. The observed bond distances and bond angles are given in Table 2. The molecular structure is illustrated in Fig. 1.

Results and Discussion

The elemental analysis of the obtained compound (*TCAEN*) corresponds to the expected one for $C_{12}H_{14}Cl_6N_2O_2$. Calcd. C = 33.44, H = 3.27, Cl = 49.36, N = 6.50. Found C = 33.28, H = 3.16, Cl = 48.9, N = 6.7. m.p. = 200–202 °C dec.

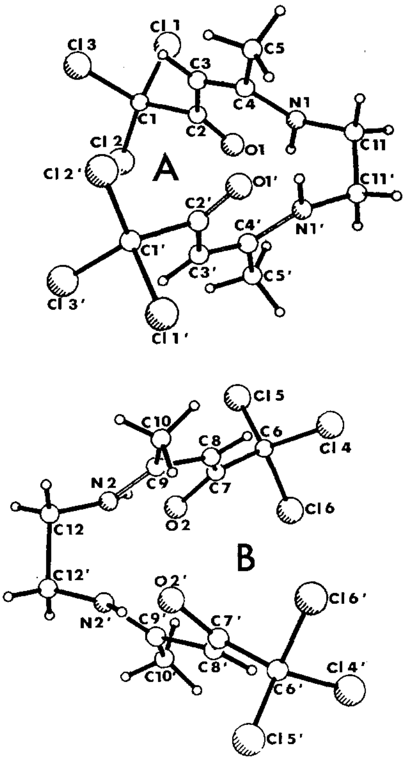

Fig. 1. Projection of the *TCAEN* molecule showing the atom labelling

The infrared spectrum is in perfect agreement with that was reported for similar *Schiff*[7,8] bases. The ^1H-NMR ($CDCl_3$): δ 2.09 s, 3.65 "pseudo-triplet", 5.78 s, 11.37 b, appears as expected and the "pseudo triplet" suggests a "fly-over" structure similar to those reported for other *Schiff* bases[8]. In the solid state an interaction of this type is unlikely, however it can not be ruled out that in solution the molecule might rotate as to leave the O(2) - - - -H(1) –N(1) and O(1)- - - -H(2) –N(2) groups in a more favourable conformation. The chemical ionization mass spectrum of *TCAEN* shows the molecular ion. Although the electronic impact mass spectrum of *TFAEN* incidates the structure[9], in *TCAEN*—due to the isotropic complexity and the absence of an CCl_3CO^+ ion—we cannot establish the CCl_3 positions in the molecule by mass spectrometry.

In order to ascertain the conformation of *TCAEN* and to obtain further information concerning its molecular geometry we carried out an X-ray crystallographic study.

Table 1. *Final fractional positional parameters* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\times 10^3$) *for non-hydrogen atoms,* $U_{eq} = (U_{11} \times U_{22} \times U_{33})^{1/3}$

Atom	x	y	z	U_{eq} (Å^2)
C(1)	8583 (8)	8999 (15)	−542 (9)	34 (3)
C(2)	8932 (8)	7748 (12)	279 (10)	37 (4)
C(3)	8757 (7)	7641 (12)	1221 (8)	23 (3)
C(4)	8902 (3)	6314 (7)	1974 (5)	29 (2)
C(5)	8572 (5)	6468 (9)	3024 (5)	48 (2)
C(6)	3700 (8)	5919 (13)	−424 (10)	35 (3)
C(7)	3995 (7)	7382 (14)	209 (7)	28 (3)
C(8)	3714 (8)	7393 (14)	1367 (8)	40 (4)
C(9)	3912 (3)	8521 (7)	1939 (4)	25 (2)
C(10)	3616 (4)	8661 (8)	3075 (5)	40 (2)
C(11)	9515 (4)	3787 (7)	2248 (5)	31 (2)
C(12)	4573 (4)	11076 (6)	2291 (4)	31 (2)
O(1)	9411 (3)	6729 (5)	−260 (4)	45 (2)
O(2)	4361 (3)	8267 (5)	−176 (3)	44 (2)
N(1)	9345 (4)	5142 (7)	1608 (5)	38 (2)
N(2)	4304 (3)	9751 (5)	1665 (3)	23 (1)
Cl(1)	7820 (1)	8349 (2)	−1387 (1)	54 (1)
Cl(2)	9450 (2)	9686 (4)	−1272 (2)	42 (1)
Cl(3)	8293 (3)	10623 (4)	208 (3)	75 (2)
Cl(4)	3289 (2)	4393 (4)	222 (3)	62 (1)
Cl(5)	2751 (2)	6614 (3)	−1317 (2)	89 (1)
Cl(6)	4410 (2)	5372 (2)	−1327 (2)	66 (1)

The X-ray structural determination shows unequivocally that the structure is the result of a nucleophilic attack on the carbonyl linked to the non-chlorinated substituent and it suggests that the electron-accepting ability of the CCl_3 group is still sufficient to induce a large $\delta +$ charge on the remote carbonyl.

TCAEN occurs in two different conformations A and B. In both, the C—C single bond and the N—H - - - -O hydrogen bond lie on and near the two-fold screw axis. As a result of this, the entire structure consists of alternated layers of A and B molecules, nearly perpendicular to the a axis.

The relevant mean values are for *TCAEN*: $\langle C(sp^3)-C(sp^3) \rangle = 1.516$ (12) Å; $\langle C(sp^3)-C(sp^2) \rangle = 1.501$ (9) Å; $\langle C(sp^2)-C(sp^2) \rangle = 1.389$ (13) Å and $\langle C=O \rangle = 1.253$ (12) Å. All these values appear standard even though some of the individual distances are some what different from their expected values.

It may be noted that the bond lengths C(3)—C(4), C(8)—C(9), C(11)—C(11′), C(12)—C(12′), and C(2)—O(1), C(7)—O(2), are affected

Table 2. *Bond lengths (Å) and angles (°); the e.s.d.'s are given in parentheses*

C(1)–C(2)	1.581 (17)	C(1)–Cl(1)	1.644 (12)
C(1)–Cl(2)	1.825 (14)	C(1)–Cl(3)	1.801 (13)
C(2)–C(3)	1.238 (16)	C(2)–O(1)	1.393 (13)
C(3)–C(4)	1.513 (12)	C(4)–C(5)	1.462 (9)
C(4)–N(1)	1.358 (9)	C(6)–C(7)	1.571 (16)
C(6)–Cl(4)	1.733 (13)	C(6)–Cl(5)	1.903 (12)
C(6)–Cl(6)	1.733 (13)	C(7)–C(8)	1.553 (14)
C(7)–O(2)	1.112 (12)	C(8)–C(9)	1.255 (13)
C(9)–C(10)	1.540 (8)	C(9)–N(2)	1.316 (8)
C(11)–N(1)	1.457 (9)	C(11)–C(11 a)	1.616 (11)
C(12)–N(2)	1.456 (7)	C(12)–C(12 a)	1.415 (12)
C(12 a)–C(12)	1.415 (12)		
C(2)–C(1)–Cl(1)	111.8 (9)	C(2)–C(1)–Cl(2)	108.7 (9)
Cl(1)–C(1)–Cl(2)	110.1 (7)	C(2)–C(1)–Cl(3)	108.3 (8)
Cl(1)–C(1)–Cl(3)	114.0 (8)	Cl(2)–C(1)–Cl(3)	103.5 (7)
Cl(1)–C(2)–C(3)	125.3 (11)	C(1)–C(2)–O(1)	108.5 (9)
C(3)–C(2)–O(1)	126.1 (10)	C(2)–C(3)–C(4)	128.2 (10)
C(3)–C(4)–C(5)	116.1 (6)	C(3)–C(4)–N(1)	116.1 (6)
C(5)–C(4)–N(1)	127.7 (6)	C(7)–C(6)–Cl(4)	121.2 (9)
C(7)–C(6)–Cl(5)	102.5 (7)	Cl(4)–C(6)–Cl(5)	102.4 (6)
C(7)–C(6)–Cl(6)	112.1 (8)	Cl(4)–C(6)–Cl(6)	112.3 (7)
Cl(5)–C(6)–Cl(6)	103.7 (6)	C(6)–C(7)–C(8)	112.2 (10)
C(6)–C(7)–O(2)	120.6 (9)	C(8)–C(7)–O(2)	127.2 (10)
C(7)–C(8)–C(9)	117.3 (10)	C(8)–C(9)–C(10)	120.6 (7)
C(8)–C(9)–N(2)	127.8 (7)	C(10)–C(9)–N(2)	111.3 (5)
N(1)–C(11)–C(11 a)	109.9 (4)	N(2)–C(12)–C(12 a)	115.3 (4)
C(4)–N(1)–C(11)	121.5 (6)	C(9)–N(2)–C(12)	130.7 (4)

by a certain amount of conjugation within the enaminoketone groups and also they seem to be sterically induced.

There is a real effect on a relative lengthening of the bond adjacent to the C–Cl bond. This lengthening being of the order of 5% of the normal $C(sp^3)-C(sp^2)$ bond length[10].

The geometry about the exocyclic C(11)–C(11′) and C(12)–C(12′) bonds is the commonly observed *gauche* conformation with torsion angles, N(1)–C(11)–C(11′)–N(1′) and N(2)–C(12)–C(12′)–N(2′) 57.3° and − 53.6°, respectively.

There is a short N----N distance of 2.92 Å and 2.91 Å for the A and B molecules in *TCAEN*. In *TCAEN* (B), there are two H----H separations shorter than 2.70 Å [H(2)----H(10C) = 2.25 Å and H(2)----H(12A) = 2.62 Å], causing some internal strain in the molecule and the N(2)–C(12)–C(12′) angle is distorted from the tetrahedral value to 115.3 (9)°. As a consequence of this, there is a little self-ring pairing of the six-membering in *TCAEN* (B) molecule.

The crystal structure is internally stabilized by two pairs of N—H----O hydrogen bonds. An intramolecular hydrogen bond links, in A, N(1) to O(1) [N(1)----O(1) = 2.738 (8) Å], N(1)—H(1) = 0.81 (9) Å, H(1)----O(1) = 1.95 (12) Å and N(1)—H(1)----O(1) = 165.2 (10)°] while in B, the interaction is between N(2) to O(2) [N(2)----O(2) = 2.662 (8) Å, N(2)—H(2) = 0.95 (9) Å, H(2)----O(2) = 1.94 (9) Å and N(2)—H(2)----O(2) = 131.8 (8)°]. Otherwise the packing is provided by *van der Waals* forces only, as revealed by the low densities. The hydrogen-bonding scheme (see Fig. 2) is identical with that observed in *TFAEN*[11] and the parent compound[12].

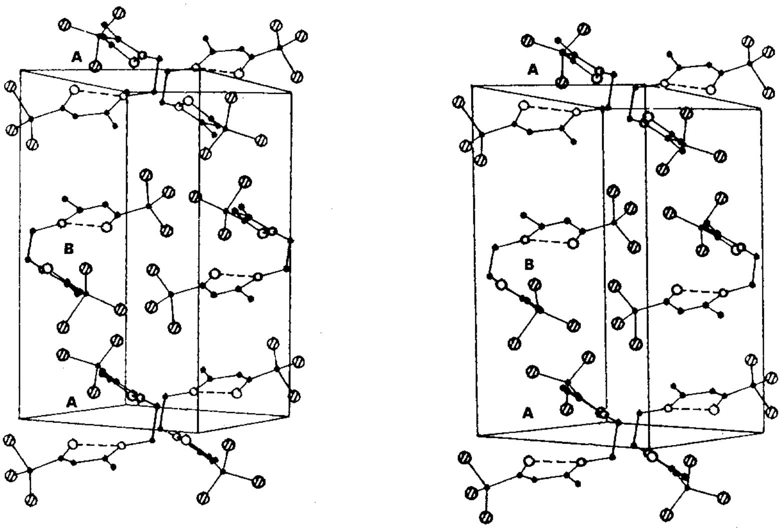

Fig. 2. Stereoscopic pair of the molecule, molecular conformation and packing showing the intramolecular hydrogen-bonding; the axial system is right-handed with the positive direction of the *b* axis towards the viewer and to the left and the *c* axis towards the viewer and to the right, with the origin at the top of the diagram

The packing of the molecules in the unit cell and the intramolecular hydrogen bonding is shown by the broken lines in the stereoscopic drawing of Fig. 2.

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