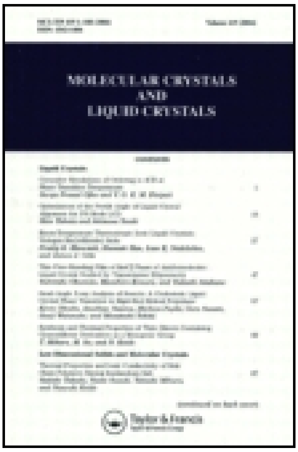

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

The Role of Chlorin—Chlorine Interaction in the Crystal structure of a Highly Volatile Molecule: Trans-3,4-Dichlorotetrahydrothiophene

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Version of record first published: 22 Sep 2006.

To cite this article: Elies Molins , Nuria Santalo , Jordi Rius , Carles Miravitlles , Concepcio Rovira & Jaume Veciana (1990): The Role of Chlorin—Chlorine Interaction in the Crystal structure of a Highly Volatile Molecule: Trans-3,4-Dichlorotetrahydrothiophene, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 187:1, 59-65

To link to this article: http://dx.doi.org/10.1080/00268949008036028

Mol. Cryst. Liq. Cryst., 1990, vol. 187, pp. 59–65
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Printed in the United States of America

THE ROLE OF CHLORINE- CHLORINE INTERACTION IN THE CRYSTAL STRUCTURE OF A HIGHLY VOLATILE MOLECULE : TRANS-3,4-DICHLOROTETRAHYDROTHIOPHENE

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Abstract The present work deals with the synthesis and spectroscopic (NMR, IR) and structural characterization of trans-3,4-dichlorotetrahydrothiophene (TDTHT). This compound is solid, but highly volatile, at room temperature and is constituted of only one conformer,in contrast with the liquid phase where both conformers coexist. The solid phase seems to be stabilized by a very short Cl...Cl interaction (∿3.3Å).

INTRODUCTION

Chlorosubstitution in aromatic molecules is an effective device for crystal engineering. Chlorine atoms bonded to an aromatic nucleus usually tend to steer the crystal structure to the so-called β-mode due to the attractive and anisotropic nature of Cl...Cl interaction. Although the directional effects of chlorine atoms have been statistically analyzed in tens of aromatic compounds,[1] extensive experimental and theoretical studies are still demanded in order to get a deeper understanding and also to control the Cl...Cl interaction in organic solids. Especially attractive are those studies concerned with Cl...Cl interactions in flexible polychlorinated molecules where other strong intermolecular interactions are absent. TDTHT is a molecule with these characteristics. It is obtained at room temperature as a highly volatile solid. This property contrasts with that shown by other related molecules (tetrahydrofurans and tetrahydrothiophenes) which are liquids. It therefore deserves deeper study.

SYNTHESIS

The synthesis procedure was described by G.W.Kilmer[2] and has been improved to yield up to 84 % of the intermediate product (trans -3,4-dihydroxotetrahydrothiophene) and up to 71 % of the final product. This was purified by crystallization in hexane giving a white solid (m.p. 58-60°C) that easily sublimes at room temperature. 3-chloro-4-hydroxotetrahydrothiophene was also been obtained as a subproduct .

X-RAY DIFFRACTION

White crystals of $C_4H_6SCl_2$ were grown by sublimation at low temperature. One suitable crystal was kept in a sealed capillary tube during indexing and data collection in order to avoid mass loss. The cell parameters are a= 6.353(5), b= 6.663(2), c= 7.594(2)Å, α= 90.06(2), β= 90.21(4), γ= 89.98(4)°, V= 321 $Å^3$. Assuming Z= 2, D_x= 1.62 $g.cm^{-3}$ and μ= 12.0 cm^{-1} for MoK_α radiation. 1121 reflections were measured over one reciprocal space hemisphere with θ< 25° ($-7\leq h\leq 7$, $-7\leq k\leq 7$, $0\leq l\leq 9$). The standard reflection decay was 0.85 %. Lorenz and polarization corrections were applied. Structure solution was carried out using Omega function[3] taking P 1 as space group.

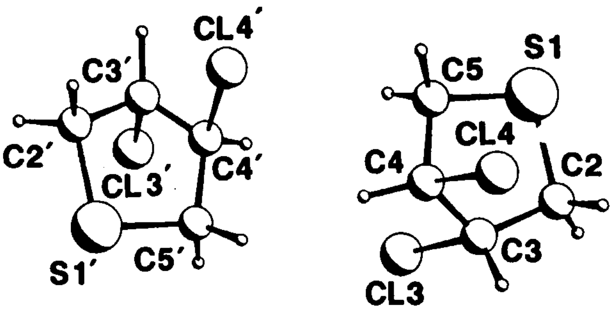

FIGURE 1 Perspective view of the asymmetric unit with the atom numbering

TABLE I Fractional atomic coordinates (x10^4) for non-hydrogen atoms with their equivalent temperature factors

Atom	x/a	y/b	z/c	B_{eq}
S1	5880	2500	-2500	6.60
CL3	1597(4)	2518(4)	-5301(3)	6.39
CL4	1614(3)	2522(4)	323(2)	6.24
C2	3913(13)	558(11)	-2540(13)	6.19
C3	1851(12)	1616(10)	-2828(14)	7.86
C4	1866(14)	3475(12)	-2398(19)	11.44
C5	3876(13)	4519(10)	-2574(12)	5.96
S1'	4342(3)	7498(4)	12493(4)	6.62
CL3'	8616(4)	7529(4)	9684(3)	6.50
CL4'	8608(3)	7525(4)	15331(2)	6.20
C2'	6270(12)	9560(11)	12416(13)	6.29
C3'	8349(12)	8515(11)	12146(15)	8.41
C4'	8364(13)	6602(11)	12583(21)	9.98
C5'	6242(12)	5513(11)	12400(12)	6.22

Refinement[4] lead to an R factor of 0.058 (R_v = 0.079, w= 1.0/(σ^2(F)+0.00908F^2)) over 965 observed reflections (I> 2.5σ(I)). Attempts to fit experimental data to higher symmetry space groups were unsuccessful. Table I lists the atomic coordinates and Figure 1 shows atom labeling for both symmetrically unrelated molecules.

The analysis of bond distances and angles indicates significant differences between the two molecules, e.g. the C2-S1-C5 angle is 92.5(3)° and that of C2'-S1'-C5', 95.8(3)°. This fact explains why both molecules are not related by a center of symmetry.

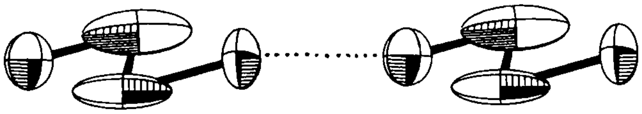

FIGURE 2 Thermal ellipsoids (33% of probability) for C3, C4, Cl3 and Cl4 atoms for two neighbour molecules. The intermolecular Cl...Cl close contact is also indicated.

TABLE II Anisotropic thermal parameters ($x10^3$) for non-hydrogen atoms with their e.s.d.'s

Atom	U11	U22	U33	U23	U13	U12
S1	43 (1)	98 (1)	109 (2)	3 (1)	8 (1)	4 (1)
CL3	89 (1)	98 (1)	56 (1)	-5 (1)	-5 (1)	-2 (1)
CL4	89 (1)	115 (2)	33 (1)	-4 (1)	7 (1)	1 (1)
C2	68 (4)	55 (4)	112 (6)	0 (4)	-6 (4)	10 (3)
C3	47 (3)	46 (3)	206 (10)	14 (5)	-13 (5)	-7 (2)
C4	40 (3)	64 (4)	330 (17)	-1 (8)	18 (6)	15 (3)
C5	74 (4)	56 (4)	96 (6)	-14 (4)	3 (4)	-2 (3)
S1'	43 (1)	93 (1)	115 (2)	0 (1)	-6 (1)	-1 (1)
CL3'	84 (1)	103 (2)	61 (1)	9 (1)	9 (1)	0 (1)
CL4'	86 (1)	114 (2)	36 (1)	6 (1)	-6 (1)	3 (1)
C2'	60 (4)	56 (4)	123 (6)	1 (4)	5 (4)	11 (3)
C3'	48 (4)	62 (4)	210 (10)	-2 (6)	16 (5)	-5 (3)
C4'	50 (4)	44 (3)	285 (13)	13 (6)	-22 (6)	-1 (3)
C5'	64 (4)	58 (4)	114 (6)	23 (4)	-4 (4)	-21 (3)

Table II lists the anisotropic thermal parameters for non-hydrogen atoms. C3, C4, C3' and C4' atoms present anomalously high values for the U_{33} coefficients. In order to clarify this point, we have depicted in Figure 2 the thermal ellipsoids of C3, C4, Cl3 and Cl4 atoms for two neighbour molecules viewed along a. Although some large vibration modes should not be surprising because of the high volatility of TDTHT, it is noticeable that the corresponding chlorine atoms vibrate less along c, probably due to their intermolecular close contact.

Two conformations are possible for the TDTHT molecule depending on the relative position of chlorine and hydrogen atoms bonded to C3 and C4 atoms. We will denote a conformer as of type A when chlorine atoms occupy axial positions and of type B when they were equatorial. From the analysis of the crystal structure we conclude that the two independent molecules belong to the same conformational type A.

Figure 3 represents crystal packing and, by a dotted line, it has been stood out the Cl3...Cl4 (3.32 Å) and the Cl3'...Cl4' (3.31 Å) contacts. The attractive nature of short intermolecular non-bonded

Cl...Cl contacts has also been pointed out in solid Cl_2, where the lowest Cl...Cl distance is 3.27Å, and in several chloro compounds such as 1,4-dichlorobenzene (3.38Å)[5]. Williams and Hsu[6] needed to incorporate an attractive potential to simulate crystal packing in solid Cl_2 and estimate that its associated partial bonding energy is 46% of the lattice energy.

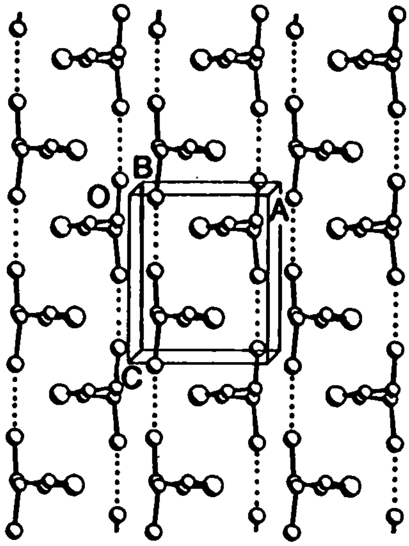

FIGURE 3 Perspective view of the crystal packing. Cl...Cl short contacts are indicated by a dotted line.

IR AND NMR SPECTRA

Figure 4 shows infrared spectra of title compound in liquid (above) and in solid phases (below). Especially noticeable is the strong band in the spectrum of the solid specimen at about 650 cm^{-1}, attributed to axial C-Cl stretching vibrations[7], that could correspond to the large thermal coefficients for C3, C4, C3' and C4' atoms mentioned above. Figure 4 also includes the uncorrected infrared frequencies for conformers A and B from MNDO calculations

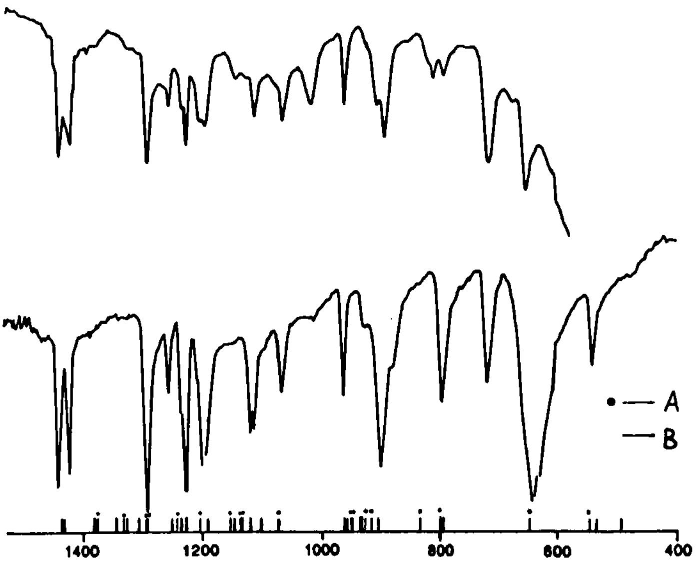

FIGURE 4 Infrared spectra of TDTHT in liquid (above) and in solid (below). Uncorrected infrared frequencies for conformers A and B are also included.

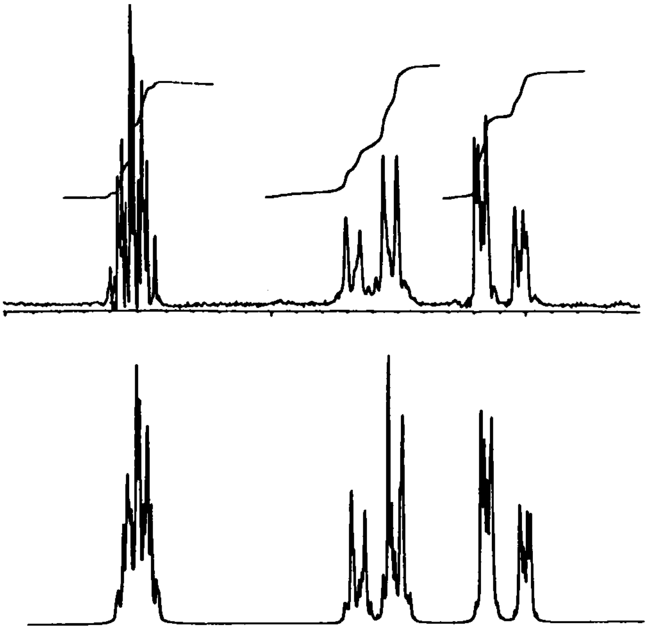

FIGURE 5 Experimental (above) and simulated (below) NMR spectra of TDTHT liquid phase.

The heats of formation obtained by MNDO for the conformers A and B are -33.29 and -33.06 Kcal/mol, respectively. The steric energy calculated by MM2 for both conformers are 11.60 and 12.09 Kcal/mol, respectively. We had previously determined the S-C-C-Cl torsion constant: $V_1 = -0.1$, $V_2 = -0.2$, $V_3 = 0.0$. All these calculations give the conformer A as the most stable in vacuum. The experimental and simulated NMR spectra of TDTHT in the liquid phase are drawn in Figure 5. The H-NMR coupling constants have been obtained using a Karplus equation on the weighted conformational populations. The good accordance with experimental data proves the coexistence of both conformers in the liquid phase.

ACKNOWLEDGEMENT

Authors would like to thank to the Programa Nacional de Nuevos Materiales, C.I.C.Y.T. (Project n. MAT 88-0268-C02) by the financial support.

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