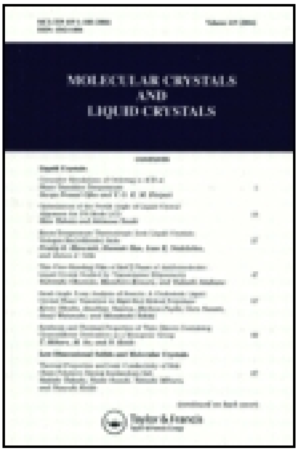

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

X-Ray Analysis and Proton Transfer Reaction in the Crystal of 2-(2′-Hydroxy-5′ -Methylphenyl)-5-Chloroben-zotriazole

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To cite this article: Aleksandra Lewanowicz & François Baert (1993): X-Ray Analysis and Proton Transfer Reaction in the Crystal of 2-(2′-Hydroxy-5′ -Methylphenyl)-5-Chloroben-zotriazole, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 229:1, 53-58

To link to this article: http://dx.doi.org/10.1080/10587259308032175

Mol. Cryst. Liq. Cryst. 1993, Vol. 229, pp. 53–58
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Printed in the United States of America

X-RAY ANALYSIS AND PROTON TRANSFER REACTION IN THE CRYSTAL OF 2-(2'-HYDROXY-5'-METHYLPHENYL)-5-CHLOROBENZOTRIAZOLE

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Abstract Preliminary results of an x-ray crystal structure of 2-(2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole at room temperature are presented as well as atomic parameters from an X-ray refinement and a TLS thermal vibration analysis on "heavy" atoms. These data allow the first step of an interpretation of the dynamics of the proton transfer reaction in this molecule.

INTRODUCTION

2-(2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole molecule (ClTIN) belongs to the class of the compounds with an intramolecular hydrogen bond which are widely used as UV stabilizers[1-6]. In such molecular systems the reaction centers are parts of the same molecule and the proton is translocated along preexisting intramolecular H-bond.

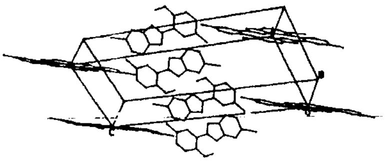
In the ClTIN molecule, the proton transfer (PT) reaction in the S_1 state takes place in non-polar environment, at 77 K[7] only. In hydrogen bonding matrices, intermolecular H-bond between the ClTIN molecule and the solvent prevents excited state prtoton transfer[7]. However, in the crystalline state at room temperature, a very broad, highly Stokes-shifted "red" fluorescence was detected. This emission has been attributed to the PT form of ClTIN[8]. In p-dibromodiphenyl matrix at room temperature, maximum of the emission spectrum of ClTIN is shifted toward short wavelength range,[9] probably because of a non-planar conformation by the molecular packing forces, like in the parent molecule TIN[10].

There are many structural requirements that control the dynamics of the intramolecular PT. It is interesting to look for a connection between molecular structure "prepared" to proton transfer reaction in the ground state and after excitation. Evidence is presented which indicates that the conformation of ClTIN molecule in the solid state is almost planar which allow the excited state proton transfer.

Experimental details were close to presented in [11, 12].

CRYSTAL STRUCTURE

X-ray studies of ClTIN were carried out at room temperature and the crystal structure was refined according to[13]. ClTIN with the formula $C_{13}H_{10}N_3OCl$ crystalizes in the monoclinic space group $P2_1/n$ with the lattice parameters a = 11.222 Å, b = 3.917 Å, c = 26.949 Å, β = 99.78° and Z = 4. Bond distances and selected angles for ClTIN molecule, calculated from fractional atomic coordinates, are presented in Table I.



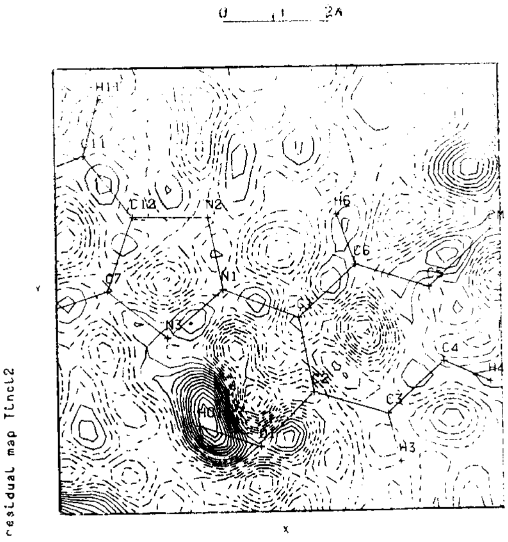


Figure 1 Crystal packing of ClTIN.

Figure 2 Electron density difference synthesis in the central part of ClTIN molecule. Substracted H atom in O-H...N bridge.

TABLE I Interatomic distances and selected angles for ClTIN (estimated standard deviations in parentheses)

Distance	r (Å)	Distance	r (Å)
C1 - C2	1.385(2)	C8 - C9	1.352(3)
C1 - C6	1.397(3)	C9 - C10	1.408(2)
C1 - N1	1.433(4)	C9 - Cl	1.754(4)
C2 - O1	1.354(3)	C10 - C11	1.347(4)
C2 - C3	1.388(4)	C11 - C12	1.408(3)
C3 - C4	1.376(3)	O1 - HO1	1.149(4)
C4 - C5	1.368(2)	C3 - H3	0.843(2)
C5 - CM	1.516(3)	C4 - H4	0.915(4)
C5 - C6	1.374(4)	CM - H1M	1.068(3)
N1 - N2	1.316(2)	CM - H2M	1.097(1)
N1 - N3	1.340(3)	CM - H3M	1.089(2)
N2 - C12	1.354(4)	C6 - H6	0.921(2)
N3 - C7	1.353(3)	C8 - H8	0.976(2)
C7 - C8	1.418(4)	C10 - H10	0.905(3)
C7 - C12	1.399(2)	C11 - H11	0.998(2)
Angles:			
C1 - C2 - O1	124.7(2)		
C2 - O1 - HO1	113.5(2)		
C2 - C1 - C6	120.5(2)		
N2 - N1 - N3	117.2(2)		
C7 - C8 - C9	114.5(2)		
C7 - C12 - C11	121.6(2)		

Numbering of the atoms according to Figure 3.

THERMAL ANALYSIS DATA

According to Hirshfeld[14] the mean square displacement amplitudes (MSDA) of a pair of non-hydrogen atoms in a typical organic molecules should be almost the same along the bond direction, though they may be widely different in other directions. From these preliminary results it may be deduced that the differences in MSDA are order 10 x 10^{-4} Å^2. Some examples are in Table II (see also Figure 3).

TABLE II Differences in MSDA values (10^4 x Δ MSDA) in $Å^2$ for "heavy" atoms in the ClTIN molecule

Atom	C1	C9	C7	N3	N2	N1	C6	C3	O1	C2
C1	-30	-51	-40	-35	-31	-63	120	-56	12	-1
C2	-29	-39	-68	-9	-43	-50	56	21	-14	
O1	11	14	-65	20	-57	-25	79	147		
C3	-48	-36	-63	-23	25	-22	15			
C6	-100	-130	-104	-159	8	-134				
N1	22	2	22	-51	-33					
N2	-98	-149	-51	-32						
N3	-12	-22	-82							
C7	11	20								
C9	56									

Displacement parameters for the cresol moiety with C6 atom are too large and it is difficult to say that this fragment of molecule seems to be less rigid. See also Figure 3.

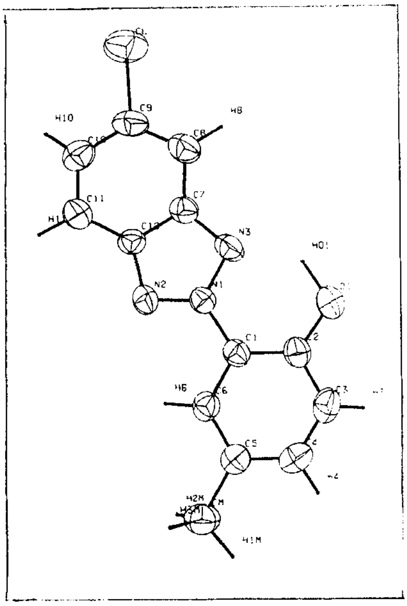


Figure 3 Conformation of crystalline ClTIN[16] with the numbering related to Table I.

RIGID-BODY MODEL

A least-squares analysis of the rigid-body motion of the molecule was carried out according to the model of Schomaker and Trueblood[15]. In the model, only U_{ij} values of the non-hydrogen atoms were fitted to the T, L and S tensors.

TABLE III Rigid-body motion parameters for all the heavy atoms

L (rad^2) x 10^{-4}			T (Å^2) x 10^{-4}			S (Årad) x 10^{-5}		
489	-41	23	4477	539	79	4	9	331
	126	4		3556	670	1	7	-165
		171			3900	-205	147	-11

R.M.S. ΔU (Å^2) 0.0044

E.S.D. 0.0049

Tensor of inertia 370.0 2813.53 3183.71

SUMMARY

The refined x-ray structural data of ClTIN lead to the conclusion that:

1° - Only one conformer is dominant in the crystalline state, however two rotameric species O-H...N are possible (rotation around central C1 - N1 bond).

2° - ClTIN molecule is practically planar in the single crystal. A very small deviation of planarity is calculated for Cl atom and for the OH- and CH_3- groups.

It is evident that within coplanar system, the proton tunneling distance is minimum and the interaction between reaction centers is maximum.

3° - The O1...N3 and H...N3 interatomic distances are equal 2.62 Å and 1.72 Å, respectively. Position of the H atom in the hydrogen bridge is well defined. The observed O-H bond is much shorter than that calculated from van der Waals contact for O...N heavy atoms (2.90 Å)[17] which is due to the rather strong intramolecular hydrogen bond.

REFERENCES

1. H.J. Heller and H.R. Blattmann, Pure Appl. Chem., 30, 145 (1972).
2. H.J. Heller and H.R. Blattmann, Pure Appl. Chem., 36, 141 (1974).
3. G. Woessner, G. Goeller, J. Rieker, H. Hoier, J.J. Stezowski, E. Daltrozzo, M. Neureiter and H.E.A. Kramer, J.Phys.Chem, 89 3629 (1985) and references therein.
4. A.L. Hudson and G.W.Scott, J.Phys.Chem., 79, 1408 (1987).
5. R.Golubski and R.Kowal, Raport Nr 13 (1987), Instytut Chemii Organicznej i Fizycznej Politechniki Wrocławskiej.
6. A.J. Chirinos Padron, J.Photochem.Photobiol. A: Chemistry, 49, 1 (1989).
7. J.Giermańska and A.Lewanowicz, Procc. of Fifth Symposium Optical Spectrocospy and Six Symposium Photochemistry, Eisenach 1988, p.18.
8. A.Lewanowicz, Materia y Konferencyjne "Kryszta y Molekularne '91", Spała 1991, p. 77.
9. A.Lewanowicz, unpublished results.
10. D.F.Bocian, A.L.Hudson and G.W.Scott, J.Chem.Phys. 79, 5802 (1983).
11. F.Baert, P.Schweis, H.G.Heger,and M.More, J.Mol.Structure, 17, 29 (1988).
12. F.Baert, J.Lamiot, C.Bochu, A.Couture and B.Mouchel, Acta Crystallog., B45, 276 (1989).
13. G.M.Sheldrick, SHELX76. Program for crystal structure determination, University of Cambridge, England (1976).
14. F.L.Hirshfeld, Acta Crystallogr. Sect.A, 36, 239 (1976).
15. V.Schomaker and K.N.Trueblood, Acta Crystallog., Sect.B, 24, 63 (1968).
16. C.K.Johnson, ORNL-3794, Oak Ridge National Laboratory, Chemistry Division, Oak Ridge, Tennessee, 1965.
17. W.C.Hamilton and I.A.Ibers in H-Bonding in Solids, (Benjamin, New York, Amsterdam, 1968), p.116.