C(8)—C(9)—C(11)	108.8 (2)	C(15)—C(16)—C(17)	106.8 (3)
C(10)—C(9)—C(11)	115.3 (2)	C(13)—C(17)—C(16)	104.3 (2)
C(1)—C(10)—C(5)	108.7 (2)	C(13)—C(17)—C(20)	115.1 (2)
C(1)—C(10)—C(9)	109.1 (2)	C(16)—C(17)—C(20)	114.8 (2)
C(1)—C(10)—C(19)	111.1 (2)	C(17)—C(20)—C(21)	117.5 (3)
C(5)—C(10)—C(9)	107.9 (2)	C(17)—C(20)—O(3)	122.3 (3)
C(5)—C(10)—C(19)	107.1 (2)	C(21)—C(20)—O(3)	120.1 (3)

C(10)—C(1)—C(2)—C(3)	−54.4 (4)
C(1)—C(2)—C(3)—C(4)	30.2 (5)
C(2)—C(3)—C(4)—C(5)	−1.3 (5)
C(3)—C(4)—C(5)—C(10)	−5.4 (5)
C(4)—C(5)—C(10)—C(1)	−17.0 (4)
C(5)—C(10)—C(1)—C(2)	46.6 (4)
C(10)—C(5)—C(6)—C(7)	−50.3 (4)
C(5)—C(6)—C(7)—C(8)	52.3 (3)
C(6)—C(7)—C(8)—C(9)	−54.7 (3)
C(7)—C(8)—C(9)—C(10)	56.6 (3)
C(8)—C(9)—C(10)—C(5)	−51.5 (3)
C(9)—C(10)—C(5)—C(6)	48.0 (3)
C(14)—C(8)—C(9)—C(11)	−51.1 (3)
C(8)—C(9)—C(11)—C(12)	53.3 (3)
C(9)—C(11)—C(12)—C(13)	−56.9 (4)
C(11)—C(12)—C(13)—C(14)	55.6 (3)
C(12)—C(13)—C(14)—C(8)	−59.9 (2)
C(13)—C(14)—C(8)—C(9)	58.7 (2)
C(17)—C(13)—C(14)—C(15)	46.3 (2)
C(13)—C(14)—C(15)—C(16)	−36.2 (3)
C(14)—C(15)—C(16)—C(17)	11.2 (3)
C(15)—C(16)—C(17)—C(13)	17.4 (3)
C(16)—C(17)—C(13)—C(14)	−38.7 (2)

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
C(1)—H(12)···O(2)	2.40 (6)	3.053 (6)	130 (5)
C(19)—H(192)···O(2)	2.43 (4)	3.035 (6)	135 (4)
C(16)—H(161)···O(1^{i})	2.76 (4)	3.490 (5)	129 (3)
C(12)—H(121)···O(2^{ii})	2.44 (4)	3.183 (6)	124 (3)

Symmetry codes: (i) $x, 1+y, z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$.

Table 3. *Puckering parameters*

Puckering parameters from Cremer & Pople (1975).

Ring *A*
$q_2 = 0.364$ Å $q_3 = 0.251$ Å
$Q = 0.442$ Å $\varphi = 11.6°$
$\theta = 55.3°$

Ring *B*
$q_2 = 0.062$ Å $q_3 = -0.530$ Å
$Q = 0.534$ Å $\varphi = 64.2°$
$\theta = 173.3°$

Ring *C*
$q_2 = 0.044$ Å $q_3 = 0.573$ Å
$Q = 0.574$ Å $\varphi = 260.2°$
$\theta = 4.4°$

Ring *D*
$q_2 = 0.456$ Å $\varphi = 193.9°$

Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985). Isotropic refinement of the structure by least-squares methods using *SHELX*76 (Sheldrick, 1976) was followed by anisotropic refinement of all the non-H atoms. All H atoms except H(213) were located from a difference Fourier map and their positions and isotropic displacement parameters were refined. H(213) was fixed geometrically.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and dihedral angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71705 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1009]

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2-(2-Hydroxy-5-methylphenyl)-5-chlorobenzotriazole, $C_{13}H_{10}ClN_3O$

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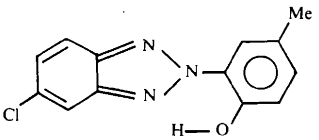
Abstract

Preliminary results of an X-ray crystal structure analysis show that the title molecule [2-(5-chloro-2-benzotriazolyl)-4-methylphenol] is practically planar in the crystalline state. There is an intramolecular hydrogen bond in which the hydroxyl group serves as a donor to the N3 atom of the benzotriazole moiety. Such systems, which undergo intramolecular proton transfer, are widely used as UV stabilizers.

Comment

The 2-(2-hydroxy-5-methylphenyl)-5-chlorobenzotriazole (Cltin) molecule belongs to a class of compounds widely used as UV absorbers and photostabilizers, properties attributed to the ability of the proton-transferred species to rapidly dissipate excitation energy (Giermanska & Lewanowicz, 1988).



Cltin

UV stabilizers undergo rapid deactivation without the emission of radiation, interconverting electronic energy into ground-state vibrational energy, which in turn is rapidly equilibrated (Werner, 1979). According to the scheme proposed by Otterstedt (1973) (*cf.* Fig. 1) the next step after the absorption of light is a proton transfer from the O atom to an N atom in the excited singlet state, followed by a fast non-destructive relaxation, namely the internal conversion. This mechanism of inhibited photochemical degradation of a molecule involves shortening the lifetime of the lowest excited state (the photoreactive state) through the transfer of energy to the O atom.

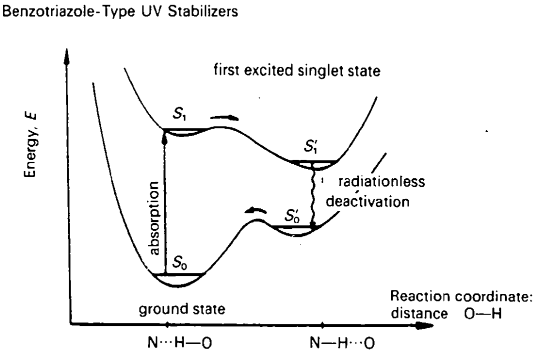


Fig. 1. Photostability: scheme of energy dissipation.

In the Cltin molecule, the proton-transfer (PT) reaction in the S_1 state (*cf.* Fig. 1) only takes place in a non-polar environment at 77 K. In the hydrogen-bonding matrices, intermolecular hydrogen bonds between the Cltin molecule and the solvent prevent excited-state proton transfer. In the crystalline state at room temperature a very broad, highly Stokes-shifted red fluorescence was detected. The appearance of this long-wavelength fluorescence (λ = 638 nm) is due to the intramolecular hydrogen bonds (Flom & Barbara, 1983; Woessner, Goeller Kollat, Stezowski, Hauser, Klein & Kramer, 1984). There are many structural requirements that control the dynamics of intramolecular proton transfer. It is interesting to look for a connection between molecular structure and the proton-transfer reaction, both in the ground state and after excitation.

The conformation of the molecule and the atomic numbering scheme are depicted in Fig. 2. The angle of intersection between the normals of the least-squares planes of the benzotriazole and the *p*-cresole moities is 1.4° (3).

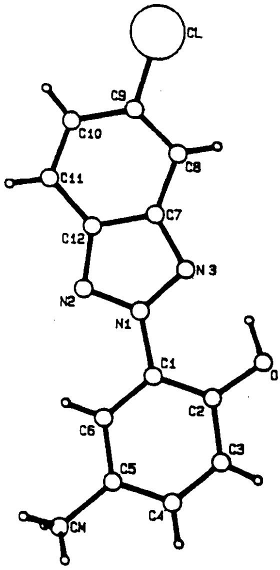


Fig. 2. Perspective view of the molecule with atomic numbering scheme.

The Cltin molecule is practically planar in the crystalline state. A very small deviation from planarity is calculated for the Cl atom and the OH and CH_3 groups. There is an intramolecular hydrogen bond in which the cresole OH group serves as the donor to atom N3 of the benzotriazole moiety (*cf.* Fig. 2). The bonding geometry [O1—HO1 = 0.90, HO1···N3 = 1.85, O1···N3 = 2.62 (7) Å, O1—HO1···N3 = 142.2 (4)°] is typical for an N···H hydrogen bond.

Experimental

Crystal data

$C_{13}H_{10}ClN_3O$
M_r = 259.68
Monoclinic
$P2_1/n$
a = 11.222 (5) Å
b = 3.917 (3) Å
c = 26.949 (7) Å
β = 98.78 (40)°
V = 1171 (1) Å^3
Z = 4

D_x = 1.47 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 2-20°
μ = 0.313 mm^{-1}
T = 293 (2) K
Needle
0.5 × 0.2 × 0.2 mm
Yellow

Data collection

Nonius CAD-4 rotating anode diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2248 measured reflections
2248 independent reflections
1043 observed reflections $[I \geq 3\sigma(I)]$

$\theta_{\max} = 20°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 3$
$l = 0 \rightarrow 25$
5 standard reflections
frequency: 120 min
intensity variation: none

Refinement

Refinement on F
$R = 0.059$
$wR = 0.059$
$S = 6.25$
1043 reflections
198 parameters
Constrained refinement of H atoms
Unit weights applied

$(\Delta/\sigma)_{\max} = 0.013$
$\Delta\rho_{\max} = 0.39$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) for non-H, Stewart, Davidson & Simpson (1965) for H

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.7564 (5)	−0.1021 (17)	0.5846 (2)	0.041 (9)
C2	0.6580 (6)	−0.2739 (18)	0.5976 (3)	0.049 (10)
O1	0.5638 (4)	−0.3933 (15)	0.5650 (2)	0.061 (7)
C3	0.6574 (6)	−0.3399 (21)	0.6481 (3)	0.066 (12)
C4	0.7523 (7)	−0.2425 (21)	0.6831 (3)	0.070 (11)
C5	0.8513 (6)	−0.0772 (18)	0.6710 (3)	0.055 (10)
CMe	0.9551 (8)	0.0300 (24)	0.7107 (3)	0.058 (12)
C6	0.8516 (6)	−0.0044 (18)	0.6213 (3)	0.051 (10)
N1	0.7628 (5)	−0.0137 (14)	0.5334 (2)	0.045 (8)
N2	0.8554 (4)	0.1503 (15)	0.5203 (2)	0.049 (8)
N3	0.6743 (4)	−0.1077 (15)	0.4966 (2)	0.039 (8)
C7	0.7146 (5)	0.0093 (17)	0.4550 (2)	0.044 (9)
C8	0.6612 (6)	−0.0110 (20)	0.4039 (3)	0.049 (11)
C9	0.7272 (6)	0.1309 (20)	0.3711 (2)	0.051 (10)
C10	0.8380 (7)	0.2958 (21)	0.3856 (3)	0.061 (11)
C11	0.8895 (6)	0.3180 (20)	0.4340 (3)	0.050 (11)
C12	0.8261 (5)	0.1704 (18)	0.4698 (2)	0.045 (9)
Cl	0.6714 (2)	0.1078 (7)	0.3070 (1)	0.084 (3)

Table 2. *Selected geometric parameters* (Å, °)

C1—C2	1.382 (9)	N1—N3	1.343 (7)
C1—C6	1.394 (9)	N2—C12	1.352 (8)
C1—N1	1.436 (8)	N3—C7	1.351 (8)
C2—O1	1.351 (8)	C7—C8	1.417 (10)
C2—C3	1.385 (10)	C7—C12	1.404 (9)
C3—C4	1.366 (11)	C8—C9	1.356 (10)
C4—C5	1.368 (10)	C9—C10	1.403 (11)
C5—CMe	1.516 (11)	C9—Cl	1.748 (7)
C5—C6	1.369 (10)	C10—C11	1.344 (10)
N1—N2	1.315 (7)	C11—C12	1.408 (9)
C2—C1—C6	120.6 (6)	C2—C1—N1	121.3 (6)
C6—C1—N1	118.1 (6)	C1—C2—O1	125.4 (6)
C1—C2—C3	117.6 (6)	O1—C2—C3	116.9 (6)
C2—C3—C4	120.5 (7)	C3—C4—C5	122.8 (7)
C4—C5—CMe	121.8 (7)	C4—C5—C6	117.1 (6)
CMe—C5—C6	121.1 (6)	C1—C6—C5	121.4 (6)
C1—N1—N2	122.2 (5)	C1—N1—N3	120.2 (5)
N2—N1—N3	117.5 (5)	N1—N2—C12	102.6 (5)
N1—N3—C7	102.5 (5)	N3—C7—C8	129.9 (6)
N3—C7—C12	108.3 (6)	C8—C7—C12	121.8 (6)
C7—C8—C9	114.8 (6)	C8—C9—C10	123.7 (7)
C8—C9—Cl	118.3 (6)	C10—C9—Cl	118.0 (6)
C9—C10—C11	122.1 (7)	C10—C11—C12	116.8 (7)
N2—C12—C7	109.2 (6)	N2—C12—C11	130.0 (6)
C7—C12—C11	120.8 (6)		

Scan width was (1.0 + 0.35tanθ)° with a prescan speed of 16.48/8° min^{-1}. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985) (50 phase sets with $E \geq 1.15$, best solution CFOM = 0.049). The non-H atoms were refined anisotropically on F (Sheldrick, 1976). H atoms were obtained from a $\Delta\rho$ synthesis, theoretically adjusted and isotropically refined.

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