Molecular Geometry. I. The Structure of Tropolonyl p-Chlorobenzoate

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Abstract: Tropolonyl p-chlorobenzoate crystallizes in the orthorhombic space group *Pbca* with $a = 10.458$ (4), $b = 16.785$ (8), and $c = 13.834$ (5) Å, $Z = 8$. Solution of the crystal structure was accomplished by the heavy atom technique. Least-squares refinement of the structure has led to a final value of the conventional R factor of 0.058 for the 1279 data having $F_o{}^2 > 2\sigma(F_o{}^2)$. The tropolone ring is planar and exhibits marked alternation of bond character. This portion of the structure is most closely formulated as a planar cycloheptatrienone rather than as a tropylium oxide.

The suggestion that tropolone and its parent, tropone, would have aromatic character[2,3] provided a stimulus for the synthesis and study of compounds that contain the cycloheptatrienone ring.[4-6] Structural studies on copper tropolonate[7] and sodium tropolonate[8,9] have shown that the seven-membered ring is planar and approximates a regular heptagon; similar results have been obtained for tropolone hydrochloride.[10] Electron diffraction studies on tropone[11] and tropolone[12,13] are in substantial agreement with these findings but possible bond alternations of 0.04 Å from a mean value of 1.41 Å are also consistent with the observed radial distribution functions.[14]

A more recent study on the structure of 2-chlorotropone suggests that there is a distinct bond alternation within the seven-membered ring.[15] Similar results were obtained from an investigation of the structure of 2-bromomethyl-2,3-dihydrofuro[2,3-*b*]tropone.[16] In view of the intense activity by theoretical chemists, who are concerned with the calculation of structural parameters of tropone, tropolone and related compounds,[17,18] we undertook a determination of the molecular structure of the p-chlorobenzoate ester of tropolone in an attempt to obtain precise structural details for comparison purposes. Figure 2 summarizes the final bond distances and angles determined for tropolonyl p-chlorobenzoate.

Experimental Section

The p-chlorobenzoate ester of tropolone was prepared by treating p-chlorobenzoyl chloride with tropolone in the presence of pyridine. The product (mp 155-157°) was recrystallized from ethanol and was obtained as thin needles elongated along the crystallographic *a* axis.

Preliminary investigation of Weissenberg and rotation photographs indicated orthorhombic symmetry and revealed the following systematic absences: $0kl$ when $k \neq 2n$, $h0l$ when $l \neq 2n$, and $hk0$ when $h \neq 2n$. These conditions are consistent with the space group $Pbca(D_{2h}{}^{15})$. The crystal density determined by flotation was 1.42 g/cm³. The calculated density corresponding to light molecules in the unit cell is 1.43 g/cm³. Unit cell parameters (21°) $a = 10.458$ (4), $b = 16.785$ (8), $c = 13.834$ (5) Å (Cu Kα, λ 1.5418 Å) were determined by a least-squares refinement of the angular parameters defining six reciprocal lattice points that has been accurately centered on a Picker FACS-I, computer assisted diffractometer.

Intensity data were collected using a θ–2θ scanning technique at a take-off angle of 2.0°. A scan interval of 2° in 2θ, automatically corrected for radiation dispersion, was used. Background measurements (10 sec) were made at each end of this interval. The scan rate was 2°/min. Aluminum foil attenuators were automatically inserted into the diffracted beam whenever the counting rate exceeded ~10,000 counts/sec. The stability of the crystal in the X-ray beam was determined by the periodic collection of three standard reflections. Subsequent analysis of these standards revealed only a minor fluctuation of intensity as a function of time. A total of 1803 unique data, to a 2θ value of 120°, was collected. These data were reduced to values of $F_o{}^2$ and $\sigma(F_o{}^2)$ by previously described methods.[19] No absorption (μ(Cu Kα) = 28.0 cm⁻¹) or extinction corrections were applied.

The structure was solved by phasing based on the coordinates of the chlorine atom as determined from a three-dimensional Patterson synthesis. All of the C and O atoms were located from the first three-dimensional Fourier synthesis. The atomic scattering factors used for Cl, C, and O are those tabulated by Hanson, Herman, Lea, and Skillman[20] while those for H were taken from Stewart, et al.[21]

Least-squares refinement based on F_o with isotropic thermal parameters gave $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.124$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2]^{1/2} = 0.146$ over the 1279 data with $F_o{}^2 \geq 2\sigma(F_o{}^2)$. Weights derived from counting statistics were of the form $w = 4F_o{}^2/\sigma^2(F_o{}^2)$. A difference Fourier computed at this stage revealed all the hydrogen atoms. These were included in the final refinement cycles with fixed, isotropic temperature factors of 4.0 Å². Two

(1) This work represents a portion of the dissertation of L. L. Reed presented to the Graduate College of the University of Arizona in partial fulfillment of the requirements for the Ph.D. degree. A detailed list of structure factors can be obtained from the thesis through *Dissertation Abstracts*.

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Table I. Atomic Coordinates[a]

Atom	x	y	z
Cl	0.0142 (1)[b]	0.4185 (1)	0.3161 (1)
O_1	0.2327 (3)	0.4433 (2)	0.8613 (2)
O_2	0.0594 (3)	0.3651 (2)	0.8449 (2)
O_3	0.2499 (3)	0.2675 (2)	0.8317 (2)
C_1	0.0471 (5)	0.4196 (2)	0.1935 (3)
C_2	0.1554 (5)	0.4571 (3)	0.1593 (4)
C_3	0.1828 (4)	0.4552 (3)	0.0639 (3)
C_4	0.1055 (4)	0.4158 (2)	0.9990 (3)
C_5	0.9954 (4)	0.3779 (3)	0.0341 (3)
C_6	0.9668 (5)	0.3799 (3)	0.1308 (3)
C_7	0.1411 (4)	0.4118 (2)	0.8977 (3)
C_8	0.0973 (4)	0.3430 (2)	0.7526 (3)
C_9	0.0254 (4)	0.3696 (3)	0.6797 (3)
C_{10}	0.0342 (5)	0.3544 (3)	0.5802 (4)
C_{11}	0.1209 (5)	0.3119 (3)	0.5309 (3)
C_{12}	0.2252 (5)	0.2699 (3)	0.5719 (4)
C_{13}	0.2597 (5)	0.2595 (3)	0.6640 (3)
C_{14}	0.2066 (4)	0.2889 (2)	0.7537 (4)
H_2[c]	0.198 (4)	0.471 (2)	0.203 (3)
H_3	0.255 (4)	0.475 (2)	0.029 (3)
H_5	0.946 (4)	0.341 (2)	0.993 (3)
H_6	0.894 (4)	0.344 (2)	0.154 (3)
H_9	0.961 (4)	0.412 (2)	0.701 (3)
H_{10}	0.987 (4)	0.383 (2)	0.544 (3)
H_{11}	0.110 (4)	0.313 (2)	0.445 (3)
H_{12}	0.273 (4)	0.240 (2)	0.523 (3)
H_{13}	0.334 (4)	0.214 (2)	0.683 (2)

[a] x, y, and z are expressed as fractional cell coordinates. The estimated standard deviation of the least significant figure is given in parentheses. [b] The estimated standard deviations, given in parentheses, were obtained from the variance–covariance matrix from the final cycle of least-squares refinement. [c] Hydrogen atoms are given the number of the carbon atoms to which they are bonded.
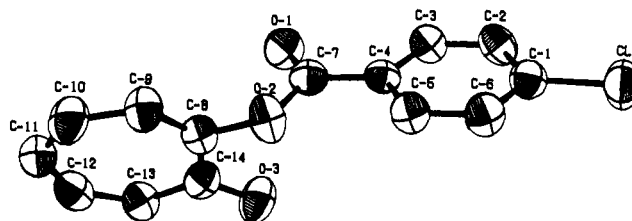
Table II. Anisotropic Thermal Parameters[a]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Cl	155 (2)	61 (1)	52 (1)	−11 (1)	13 (1)	−2 (1)
O_1	97 (4)	47 (1)	70 (2)	−17 (2)	23 (2)	1 (1)
O_2	62 (3)	60 (2)	53 (2)	−6 (2)	5 (2)	−12 (1)
O_3	129 (4)	63 (2)	59 (2)	20 (2)	−9 (3)	14 (2)
C_1	89 (5)	36 (2)	57 (3)	−2 (3)	3 (3)	−1 (2)
C_2	91 (6)	44 (2)	61 (4)	−6 (3)	−11 (4)	−12 (2)
C_3	75 (5)	40 (2)	58 (3)	−7 (3)	8 (3)	−6 (2)
C_4	66 (4)	29 (2)	53 (3)	3 (2)	4 (3)	−2 (2)
C_5	70 (5)	42 (2)	55 (3)	−10 (3)	1 (3)	−4 (2)
C_6	83 (5)	46 (2)	62 (3)	−14 (3)	10 (3)	−2 (2)
C_7	78 (5)	32 (2)	58 (3)	10 (3)	0 (3)	1 (2)
C_8	71 (5)	38 (2)	50 (3)	−4 (2)	2 (3)	−2 (2)
C_9	86 (6)	50 (2)	55 (3)	10 (3)	−3 (3)	−2 (2)
C_{10}	126 (7)	57 (3)	64 (4)	14 (3)	−23 (4)	7 (2)
C_{11}	139 (7)	45 (2)	52 (3)	−3 (4)	−3 (4)	−1 (2)
C_{12}	97 (6)	45 (2)	62 (3)	−13 (3)	25 (4)	−10 (2)
C_{13}	90 (5)	44 (2)	61 (3)	2 (3)	7 (4)	−3 (2)
C_{14}	84 (5)	39 (2)	56 (3)	−4 (3)	1 (3)	5 (2)
H[b]						

[a] The general anisotropic temperature factor has the form $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] Hydrogen atoms were assigned a fixed isotropic temperature factor of 4.0 Å².

final refinement cycles using individual atom anisotropic thermal parameters gave $R_1 = 0.058$, and $R_2 = 0.065$. A final structure factor calculation over all 1803 data gave $R_1 = 0.084$ and $R_2 = 0.068$.[22] A final difference electron density map was calculated based on the 1279 data used in refinement. The maximum residual electron density was 0.42 e/Å³.

(22) Programs used in this investigation include Zalkin's FORDAP Fourier program, Busing's ORFFE and ORFLS programs (W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory, Oak Ridge, Tenn.), and Johnson's ORTEP plotting program. The necessary computations were performed at the University of Arizona Computer Center on a CDC 6400 computer.

Figure 1. Perspective view of tropolonyl p-chlorobenzoate. The view is down the −a axis.

Results and Discussion

Table I shows the final atomic coordinates and Table II the anisotropic thermal parameters for the molecule. Bond distances and angles are recorded in Tables III and IV, respectively. Figure 1 depicts the

Table III. Bond Distances

Bond	Bond distance, Å	Bond	Bond distance, A
$Cl-C_1$	1.730 (4)	C_9-H_9	1.02 (4)
C_1-C_2	1.380 (6)	C_8-O_2	1.388 (5)
C_1-C_6	1.378 (6)	C_8-C_9	1.336 (6)
C_2-C_3	1.350 (6)	C_9-C_{10}	1.403 (7)
C_3-C_4	1.379 (6)	$C_{10}-C_{11}$	1.341 (7)
C_4-C_5	1.402 (6)	$C_{11}-C_{12}$	1.417 (7)
C_4-C_7	1.452 (6)	$C_{12}-C_{13}$	1.336 (6)
C_5-C_6	1.371 (6)	$C_{13}-C_{14}$	1.447 (6)
C_7-O_1	1.205 (5)	$C_{14}-O_3$	1.225 (5)
C_7-O_2	1.371 (5)	$C_{14}-C_8$	1.459 (6)
C_2-H_2	0.78 (4)	$C_{10}-H_{10}$	0.85 (4)
C_3-H_3	0.95 (4)	$C_{11}-H_{11}$	1.19 (4)
C_5-H_5	0.99 (4)	$C_{12}-H_{12}$	0.98 (4)
C_6-H_6	1.03 (4)	$C_{13}-H_{13}$	1.12 (4)

Table IV. Bond Angles

Atoms	Bond angle, deg	Atoms	Bond angle, deg
$Cl-C_1-C_2$	120.2 (4)	$C_{13}-C_{14}-O_3$	120.9 (4)
$Cl-C_1-C_6$	119.4 (4)	$C_{14}-C_6-O_2$	112.4 (4)
$O_1-C_7-O_2$	121.6 (4)	$C_{14}-C_8-C_9$	131.0 (4)
$C_1-C_2-C_3$	120.0 (4)	$C_1-C_2-H_2$	110 (3)
$C_2-C_3-C_4$	121.5 (5)	$H_2-C_2-C_3$	130 (3)
$C_3-C_4-C_5$	118.3 (4)	$C_2-C_3-H_3$	131 (2)
$C_3-C_4-C_7$	120.0 (4)	$H_3-C_3-C_4$	107 (2)
$C_4-C_5-C_6$	120.4 (4)	$C_4-C_5-H_5$	121 (2)
$C_4-C_7-O_1$	126.0 (4)	$H_5-C_5-C_6$	118 (2)
$C_4-C_7-O_2$	112.4 (4)	$C_5-C_6-H_6$	117 (2)
$C_5-C_4-C_7$	121.6 (4)	$H_6-C_6-C_1$	122 (2)
$C_5-C_6-C_1$	119.6 (4)	$C_8-C_9-H_9$	113 (2)
$C_6-C_1-C_2$	120.3 (4)	$H_9-C_9-C_{10}$	117 (2)
$C_7-O_4-C_8$	117.7 (3)	$C_9-C_{10}-H_{10}$	116 (3)
$C_6-C_9-C_{10}$	130.1 (5)	$H_{10}-C_{10}-C_{11}$	113 (3)
$C_6-C_{14}-O_3$	118.8 (4)	$C_{10}-C_{11}-H_{11}$	116 (2)
$C_9-C_8-O_2$	116.4 (4)	$H_{11}-C_{11}-C_{12}$	119 (2)
$C_9-C_{10}-C_{11}$	129.8 (5)	$C_{11}-C_{12}-H_{12}$	110 (2)
$C_{10}-C_{11}-C_{12}$	125.6 (5)	$H_{12}-C_{12}-C_{13}$	119 (2)
$C_{11}-C_{12}-C_{13}$	130.9 (5)	$C_{12}-C_{13}-H_{13}$	120 (2)
$C_{12}-C_{13}-C_{14}$	132.1 (5)	$H_{13}-C_{13}-C_{14}$	107 (2)
$C_{13}-C_{14}-C_8$	120.3 (4)	$H_{13}-C_{13}-C_{14}$	107 (2)

molecule as viewed in projection (100) and includes the atomic numbering scheme used.

A least-squares plane was calculated through the benzene ring and the equation describing this plane, with respect to the crystallographic (orthogonal) axes, is $-0.5265X + 0.8388Y - 0.1387Z = 5.312$. The maximum deviation from this plane was -0.004 Å for

Figure 2. Bond distances and angles for tropolonyl p-chlorobenzoate.

C3. Small displacements were found for the chlorine (0.069 Å) and the ester group (C7, 0.063; O1, 0.050; O2, 0.170 Å). A least-squares plane was also calculated through the carbon atoms of the seven-membered ring and the equation of the plane for this ring is $0.5907X + 0.8030Y - 0.0790Z = 4.378$. Displacements from this plane were small (C8, 0.022; C9, 0.016; C10, −0.024; C11, −0.009; C12, 0.029; C13, −0.001; C14, −0.032; O2, −0.014 Å). Oxygen 3 was displaced −0.136 Å from the mean plane of the heptagon.

The most interesting feature of the structure is the distinct alternation of bond character in the seven-membered ring. From a consideration of the observed bond lengths it appears that this ring more closely resembles a cycloheptatrienone structure rather than a tropylium oxide.

The average C–C distance in the phenyl ring is 1.375 (15) Å which compares favorably with the generally accepted value of 1.392 (10) Å[23] for benzene. A realistic value for the standard deviation associated with a bond length (excluding hydrogens) in this structure is probably 0.010 Å. If this order of experimental error is conceded, then the bond alternation that is observed in the tropolone ring falls well outside the range of experimental error ($\geq 3\sigma$).

The length of the C–O bond (1.225 (5) Å) in the seven-membered ring is in excellent agreement with the values found in X-ray diffraction studies of 2-chlorotropone (1.23 (2) Å)[15] and 2-bromomethyl-2,3-dihydrofuro[2,3-b]tropone (1.232 (11) Å).[15] Similar values were found for cyclohexanone (1.24 (2) Å) and 2-methylcyclohexanone (1.24 (2) Å) as determined by electron diffraction methods.[24] Carbon–carbon single bonds (C13–C14, 1.447 (6); C14–C8, 1.459 (6) Å) compare well with 1.48–1.50 Å for the C_{sp^2}–C_{sp^2} single bond.[25] These results coupled with the fact that O3 lies significantly out of the plane of the heptagon (−0.136 Å) indicate that the carbonyl group of the tropolone ring is normal and is not well represented by the resonance

form $>C^+$–O^-. This conclusion is supported by consideration of the dipole moments of cycloheptanone (3.04 D),[26] tropolone (3.71 D),[27] and 1,2-cycloheptanedione (3.74 D).[28] Bonds C8–C9, C10–C11, C12–C13 (1.336 (6), 1.341 (7), 1.336 (6) Å) compare with 1.337 (6) Å[29] for a carbon–carbon double bond. The remaining bonds C9–C10 and C11–C12 (1.403 (7), 1.417 (7) Å) represent significantly shortened C_{sp^2}–C_{sp^2} single bonds. Similar results were reported for 2-chlorotropone[15] and 2-bromomethyl-2,3-dihydrofuro[2,3-b]tropone.[16]

The C8–O2 bond (1.388 (5) Å) is considerably longer than that observed for tropolone (1.34 Å).[13] This is quite reasonable since the oxygen is part of an ester group and the unshared electrons on oxygen are relatively unavailable for delocalization in the seven-membered ring. In terms of resonance structures, it would appear that canonical forms such as 1a do not contribute

to the resonance hybrid to any significant extent. This is in contrast to observations on 2-bromomethyl-2,3-dihydrofuro[2,3-b]tropone[16] where forms analogous to 1a are suggested to be important contributors to the resonance hybrid.

Figure 2 shows the final bond distances and angles for the molecule and Figure 3 a stereoscopic view of the contents of a unit cell.

Figure 3. Stereoscopic view of the contents of a unit cell. The cell, viewed down −a, has c horizontal and b vertical.

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