TRANS-2-(P-TOLYL)CYCLOPROPANOIC ACID

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Phenyl Substituted Cyclopropanes. I. *trans*-2-(*p*-Tolyl)cyclopropanoic acid

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Abstract. $C_{11}H_{12}O_2$, $M_r = 176 \cdot 215$, orthorhombic, *Pbcn*, $a = 22 \cdot 197$ (4), $b = 10 \cdot 104$ (2), $c = 8 \cdot 595$ (2) Å, $V = 1927 \cdot 7$ Å^3, $Z = 8$, $D_m = 1 \cdot 18$, $D_x = 1 \cdot 214$ g cm^{-3}; λ(Mo $K\alpha$) = $0 \cdot 71069$ Å, $\mu = 0 \cdot 047$ mm^{-1}, $F(000) = 752$, $T = 298$ K, $R = 0 \cdot 067$ and $wR = 0 \cdot 074$ for 689 unique reflections with $I > 3\sigma(I)$. The crystal structure consists of cyclic—COOH hydrogen-bonded dimers arranged along *a* with the H atoms situated on a twofold axis equidistant from pairs of O atoms. The *p*-tolyl and carboxylate groups adopt bisected positions with respect to the cyclopropyl ring. The observed pattern of ring bond lengths is consistent with conjugative π-acceptor interactions involving asymmetry parameters δ(tolyl) = $-0 \cdot 009$ and δ(COOH) = $-0 \cdot 026$ Å.

Introduction. The physical and chemical properties and reactivity patterns of cyclopropane are atypical of higher cycloalkanes. Spectroscopic and chemical studies of various substituted cyclopropanes have shown that the cyclopropyl ring is similar to a double bond in many aspects (Deno, Richey, Liu, Lincoln & Turner, 1965; Schleyer & Buss, 1969; Charton, 1970). The ability of cyclopropane to conjugate with adjacent π acceptors, *e.g.* carbonyl, cyano, *etc.* (Hoffmann, 1970; Hoffmann & Stohrer, 1971), and its highly effective stabilization of carbonium ions (Deno, Richey, Liu, Lincoln & Turner, 1965; Schleyer & Buss, 1969) are of particular interest to chemists. The effect of substitution on the geometry of cyclopropane has generated widespread interest and numerous theoretical and experimental studies. In particular, for π-acceptor substituents, the distal ring bond is shortened and vicinal bonds are lengthened. Data for electron-donor substituents are sparse, and the conjugative effect of some substituents are not yet clearly defined (Allen, 1980, 1981). In the case of phenyl substituents they appear to accept electron density from the cyclopropane 3*e'* orbitals in the bisected conformation, but to donate electron density to the 4*e'* orbitals in the (predominant) perpendicular conformation.

This paper presents the X-ray structure of the first of a series of phenylcyclopropanes, undertaken in order to understand the complex conjugative interaction between a phenyl substituent and the cyclopropane ring.

Experimental. Density determined by flotation in CCl_4/n-hexane. Colourless cube, $0 \cdot 48 \times 0 \cdot 42 \times 0 \cdot 48$ mm. Automated four-circle Philips PW 1100 diffractometer. Lattice parameters determined by least-squares procedure applied to the setting angles of 25 strong reflections in the range $6 \cdot 6 < \theta < 9 \cdot 3°$. Intensity data to $(\sin\theta)/\lambda = 0 \cdot 55$ Å^{-1} in the range $0 \leq h \leq 26$, $0 \leq k \leq 11$, $0 \leq l \leq 9$ measured with graphite monochromated Mo $K\alpha$ radiation; intensities measured by ▨▨ scans. ▨▨ standards θ monitored every ▨▨ reflections; intensity variation ▨▨. Systematic absences proved the space group to be *Pbcn*. After Lp corrections the 1378 initial reflections were reduced to 689 unique data with $I > 3\sigma(I)$. No corrections made for absorption or extinction. Structure solved by direct methods using *SHELX77* (Sheldrick, 1977) and refined by full-matrix least squares. All H atoms were placed in positions derived from a difference Fourier map and C—H were refined using a riding model and with one overall isotropic temperature factor. The two O—H were treated at $0, y, 0 \cdot 25$; one *y* coordinate was refined but the other was held fixed during refinement. All non-H atoms were refined anisotropically. Final refinement converged to $R = 0 \cdot 067$ and $wR = 0 \cdot 074$ with $(\Delta/\sigma)_{max} = 0 \cdot 026$. Maximum and minimum heights in final difference Fourier synthesis were $+0 \cdot 18$ and $-0 \cdot 24$ e Å^{-3}. Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). The function minimized was $\Sigma(|F_o| - |F_c|)^2$ where $w = 1/[\sigma^2(F_o) + gF_o^2]$ and g was set to $0 \cdot 0008$. All calculations performed with *SHELX77* (Sheldrick, 1977) on a Burroughs B 5900 computer at the Universidad de Los Andes.

Discussion. Positional and isotropic thermal parameters and the resulting bond lengths and angles are given in Tables 1 and 2, respectively.* The crystal structure of *trans*-2-(*p*-tolyl)cyclopropanoic acid consists of hydrogen-bonded dimers (Fig. 1) having C_2 symmetry. The molecules in the unit cell are arranged along **a**, with the H-atoms involved in dimer formation lying on the twofold crystallographic axis (Fig. 2). The H atoms forming the dimer have O—H distances of 1·30 (4) Å, O—H—O angles of 164 and 176° respectively and O···O distances of 2·602 (8) and 2·583 (8) Å.

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* Lists of anisotropic thermal parameters, H-atom coordinates, selected non-bonded distances, mean-plane calculations, selected dihedral angles, torsion angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52504 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The carboxylic and *p*-tolyl groups both adopt bisected conformations with torsion angles $X(1)$—C(1)—C(4)—O(1) and $X(2)$—C(2)—C(5)—C(6) of −5·1 and −175·3° respectively, where $X(1)$ and $X(2)$ are the midpoints of the relevant distal bonds.

The C=O bonds of the carboxylate group are equal to within 2σ, [C(4)—O(1) = 1·262 (6) and C(4)—O(2) = 1·253 (7) Å], a feature indicating complete electron delocalization. The tolyl group angles and bond distances are in the expected range.

Tables 1 & 2, Figs 1 & 2 HERE

The bond lengths observed for the cyclopropyl ring (I) can be explained by assuming additivity of bond length asymmetries, a principle found to be applicable for pure acceptor substitution (Allen, 1980). The mean C—C distance in the three-membered ring d_Δ is 1·496 (8) Å. The distal bond shortening due to the *p*-tolyl substituent [δ_1 in (I)] is −0·009 Å and δ_2 for the carboxylic group is −0·026 Å. The latter value agrees with the reported mean value for carbonyl groups, $\delta(C{=}O) = -0.026$ (5) Å (Allen, 1980), but the δ_1-value obtained for the *p*-tolyl substituent is somewhat smaller than that reported for phenyl groups [−0·018 (2) Å]. The precision obtained for present structure is not high enough to establish firmly that δ(tolyl) is smaller than δ(phenyl) and further work is required to examine this possibility. We note that *E*-2-*p*-nitrophenylcyclopropyl methyl ketone (Bordner, Jones & Johnson, 1972), to our knowledge the only compound so far reported with a similar asymmetry pattern of cyclopropyl bond lengths (1·51, 1·49 and 1·48 Å), yields $\delta(C{=}O) = -0.026$ Å and $\delta(PhNO_2) = -0.017$ Å. The latter is larger than our δ_1 value, and both values are similar to the reported values for $\delta(C{=}O)$ and $\delta(Ph)$ (Allen, 1980).

Formula 1 Here

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Table 1. *Atomic co-ordinates* ($\times 10^4$) *with e.s.d.'s in parentheses and isotropic temperature factors* ($\mathring{A}^2 \times 10^3$)

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}
C(1)	1308 (3)	2829 (6)	529 (8)	67
C(2)	1728 (3)	4001 (5)	663 (8)	64
C(3)	1387 (3)	3787 (7)	−787 (8)	76
C(4)	745 (3)	2849 (6)	1407 (8)	63
C(5)	2392 (2)	3779 (6)	732 (7)	60
C(6)	2736 (3)	4548 (6)	1724 (8)	66
C(7)	3349 (3)	4364 (7)	1820 (9)	75
C(8)	3636 (3)	3418 (8)	956 (9)	79
C(9)	3297 (3)	2658 (7)	−17 (9)	79
C(10)	2677 (3)	2827 (7)	−142 (8)	73
C(11)	4307 (3)	3188 (9)	1179 (13)	122
O(1)	502 (2)	3947 (4)	1719 (6)	93
O(2)	512 (2)	1767 (4)	1785 (6)	86

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(2)—C(1)	1·513 (8)	C(3)—C(1)	1·499 (8)	
C(4)—C(1)	1·459 (8)	C(3)—C(2)	1·474 (8)	
C(5)—C(2)	1·491 (7)	O(1)—C(4)	1·262 (6)	
O(2)—C(4)	1·253 (7)	C(6)—C(5)	1·383 (8)	
C(10)—C(5)	1·375 (8)	C(7)—C(6)	1·376 (8)	
C(8)—C(7)	1·368 (9)	C(9)—C(8)	1·361 (9)	
C(11)—C(8)	1·521 (10)	C(10)—C(9)	1·390 (9)	

C(3)—C(1)—C(2)	58·6 (4)	C(4)—C(1)—C(2)	118·5 (5)
C(4)—C(1)—C(3)	118·8 (6)	C(3)—C(2)—C(1)	60·2 (4)
C(5)—C(2)—C(1)	119·7 (5)	C(5)—C(2)—C(3)	121·3 (6)
C(2)—C(3)—C(1)	61·1 (4)	O(1)—C(4)—C(1)	119·2 (6)
O(2)—C(4)—C(1)	118·4 (6)	O(2)—C(4)—O(1)	122·3 (6)
C(6)—C(5)—C(2)	119·1 (6)	C(10)—C(5)—C(2)	122·6 (6)
C(10)—C(5)—C(6)	118·3 (5)	C(7)—C(6)—C(5)	120·5 (6)
C(8)—C(7)—C(6)	121·4 (6)	C(9)—C(8)—C(7)	118·1 (6)
C(11)—C(8)—C(7)	119·6 (8)	C(11)—C(8)—C(9)	122·2 (8)
C(10)—C(9)—C(8)	121·6 (7)	C(9)—C(10)—C(5)	120·0 (6)

Fig. 1. Perspective view of the molecule showing the atomic labelling scheme.

Fig. 2. (001) projection of the unit cell.

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Formula 1.

Fig. 1

Fig. 2