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Phenyl-Substituted Cyclopropanes. II. Ethyl *trans*-2-Phenylcyclopropane-1-carboxylate

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Abstract. $C_{12}H_{14}O_2$, $M_r = 190{\cdot}24$, orthorhombic, $Pca2_1$, $a = 6{\cdot}931\,(2)$, $b = 7{\cdot}708\,(2)$, $c = 20{\cdot}288\,(4)$ Å, $V = 1084$ Å^3, $Z = 4$, $D_x = 1{\cdot}17$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}73$ cm^{-1}, $F(000) = 408$, $T = 298$ K, $R = 0{\cdot}078$ for 398 unique reflections. The ester substituent adopts a *cis*-bisected conformation with the carbonyl oxygen eclipsing the ring. The phenyl substituent also adopts the bisected conformation and, hence, competes with the ester group in conjugative interactions with the cyclopropane ring. Ring bond lengths are equal at 1·50 (2), 1·50 (2), 1·51 (2) Å, the high e.s.d.'s being due to limitations placed on the room-temperature data set by the low melting point (311–312 K).

Introduction. The interaction between a cyclopropane ring and an appropriately oriented π-acceptor substituent, *e.g.* a carbonyl group, shortens the distal bond opposite the substituent and lengthens the vicinal bonds. Data for electron-donor substituents are sparse and their effects on the ring are not clearly defined. In the case of phenyl substituents they appear to accept electron density from the cyclopropane $3e'$ orbitals in the bisected conformation, but to donate electron density to the $4e'$ orbitals in the predominant perpendicular conformation (Allen, 1980). The many reported structures of phenylcyclopropanes are mostly heavily substituted (Yamamoto, Sakai, Ohta, Matsuzaki & Fukuyama, 1985; Tinant, Wu, Declercq, Van Meerssche, De Mesmaeker, Masamba, Merenyi & Viehe, 1985; Poppleton, 1986; Allen, 1980, and references therein). In these structures, along with the electronic interaction, there is always an added steric effect between the phenyl group and other substituents. We are currently examining some phenylcyclopropanes which exhibit minimum steric effects in order to understand the complex electronic interactions in phenyl-substituted cyclopropanes.

Here we report the structure of ethyl *trans*-2-phenylcyclopropane-1-carboxylate which, together with (*E*)-2-(*p*-nitrophenyl)cyclopropyl methyl ketone (Bordner, Jones & Johnson, 1972) and *trans*-2-(*p*-tolyl)cyclopropanoic acid (Ramírez, Rivera, Rodulfo de Gil, Alonso & Pékerar, 1990), are the only reported phenylcyclopropanes in the crystalline state with minimal steric effects. Consequently, the phenyl substituent might be expected to adopt the energetically preferred conformation.

Experimental. Elongated white prisms were grown from ether:hexane. Crystal 0·32 × 0·35 × 0·26 mm sealed in a Lindemann tube. Automated four-circle Philips PW 1100 diffractometer. Lattice parameters

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Table 1. *Atomic coordinates* ($\times 10^3$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$)

	x	y	z	U_{eq}/U_{iso}
C(1)	76 (2)	915 (1)	−71 (1)	54 (3)
C(2)	183 (2)	756 (2)	−47 (1)	55 (3)
C(3)	−33 (2)	754 (2)	−53 (1)	75 (3)
C(4)	91 (2)	958 (2)	−143 (1)	56 (3)
C(5)	102 (2)	1189 (2)	−220 (1)	84 (3)
C(6)	72 (3)	1368 (2)	−222 (1)	145*
C(7)	272 (2)	755 (1)	19 (1)	45 (2)
C(8)	196 (2)	844 (2)	72 (1)	61 (3)
C(9)	290 (2)	832 (2)	133 (1)	78 (3)
C(10)	448 (2)	743 (2)	142 (1)	78 (3)
C(11)	534 (2)	657 (2)	88 (1)	78 (3)
C(12)	444 (2)	668 (2)	28 (1)	56 (3)
O(1)	101 (1)	853 (1)	−186	83*
O(2)	89 (1)	1131 (1)	−151 (1)	64*

* Anisotropic temperature factors. $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j^*$.

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

C(2)—C(1)	1·51 (2)	C(3)—C(1)	1·50 (2)
C(4)—C(1)	1·49 (2)	C(3)—C(2)	1·50 (2)
C(7)—C(2)	1·48 (1)	O(1)—C(4)	1·20 (1)
O(2)—C(4)	1·34 (1)	C(5)—O(2)	1·47 (2)
C(6)—C(5)	1·39 (2)	C(8)—C(7)	1·38 (2)
C(12)—C(7)	1·37 (1)	C(9)—C(8)	1·40 (2)
C(10)—C(9)	1·31 (2)	C(11)—C(10)	1·42 (2)
C(12)—C(11)	1·38 (2)		

C(3)—C(1)—C(2)	60 (1)	C(4)—C(1)—C(2)	118 (1)
C(4)—C(1)—C(3)	117 (1)	C(3)—C(2)—C(1)	60 (1)
C(7)—C(2)—C(1)	120 (1)	C(7)—C(2)—C(3)	120 (1)
C(2)—C(3)—C(1)	61 (1)	O(1)—C(4)—C(1)	125 (1)
O(2)—C(4)—C(1)	110 (1)	O(2)—C(4)—O(1)	126 (1)
C(5)—O(2)—C(4)	115 (1)	C(6)—C(5)—O(2)	109 (1)
C(8)—C(7)—C(2)	123 (1)	C(12)—C(7)—C(2)	119 (1)
C(12)—C(7)—C(8)	118 (1)	C(9)—C(8)—C(7)	118 (1)
C(10)—C(9)—C(8)	123 (1)	C(11)—C(10)—C(9)	120 (1)
C(12)—C(11)—C(10)	118 (1)	C(11)—C(12)—C(7)	123 (1)

determined by least-squares procedure applied to the setting angles of 25 strong reflections in the range $4{\cdot}43 < \theta < 27{\cdot}65°$. Intensity data to $(\sin\theta)/\lambda = 0{\cdot}653$ Å^{-1} ($0 \le h \le 8$, $0 \le k \le 9$, $0 \le l \le 24$) measured with graphite-monochromated (Mo $K\alpha$) radiation; intensities measured by θ–2θ scans. Three standards monitored every 50 reflections; intensity variation <4%. Systematic absences proved the space group to be $Pca2_1$. After Lp corrections the initial 952 reflections were reduced to 398 unique observed data with $I > 3\sigma(I)$. No corrections for absorption or extinction. Structure solved by direct methods using *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977) with part of the geometry of the molecule taken into account to calculate the E values. The structure refined by full-matrix least squares, with isotropic temperature factors for all non-H atoms, converged to $R = 0{\cdot}100$. H atoms were placed in positions observed in a difference Fourier map, except those on the terminal CH_3 group, which were placed in calculated positions. All H atoms were refined as rigid groups, with the constraint that all C—H = 1·00 Å, and with one overall temperature factor. Non-H atoms were refined isotropically, except O(1), O(2) and C(6) which were refined anisotropically. Final refinement converged to $R = 0{\cdot}078$ and $wR = 0{\cdot}077$ with $(\Delta/\sigma)_{max} = 0{\cdot}028$. $S = 2{\cdot}47$. Max. and min. heights in final difference Fourier synthesis were $+0{\cdot}28$ and $-0{\cdot}24$ e Å^{-3}. Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma^2(F_o) + 0{\cdot}0190F_o^2]$. All calculations performed with the *SHELX*77 system (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 consists of discrete molecules (Fig. 1.) aligned along c and held together only through van der Waals forces (Fig. 2). This fragile molecular packing, reflected in the low melting point (311–312 K), gives limited diffraction data and high

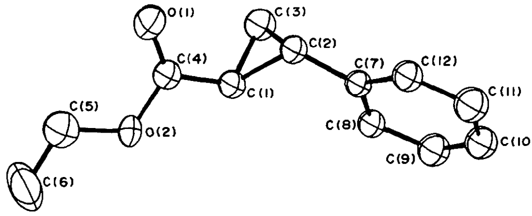

Fig. 1. Perspective view of the molecule showing the atomic labelling.

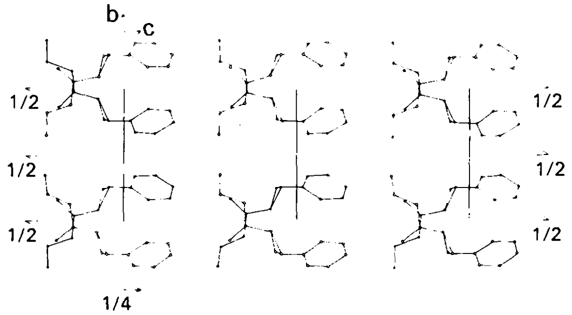

Fig. 2. (100) projection of the unit cell.

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* Lists of anisotropic thermal parameters, H-atom coordinates, H-atom bond lengths, hydrogen-bond angles, selected non-bonded distances, mean-plane calculations, selected torsion angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53582 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

e.s.d.'s in the positional and thermal parameters. The ester group adopts a *cis* bisected conformation with torsion angle a X(1)—C(1)—C(4)—O(1) of 1(1)°; X(1) is the midpoint of C(2)—C(3), distal to C(1) as defined by Allen (1980). This conformation allows optimum conjugation between the C=O of the ester group and the cyclopropane ring. The phenyl substituent adopts the bisected conformation with a torsion angle X(2)—C(2)—C(7)—C(8) of −2(1)°; X(2) is the midpoint of C(1)—C(3), distal to C(2). Sterically similar derivatives such as *trans*-2-(*p*-tolyl)cyclopropanoic acid (Ramírez *et al.*, 1990) and *trans*-(*p*-nitrophenyl)cyclopropyl methyl ketone (Bordner *et al.*, 1972) also exhibit this conformation (the torsion angle is 5·1 and 4·8°, respectively). Thus, both phenyl and ester groups withdraw electron density from the cyclopropane ring. These electronic interactions should induce an asymmetric pattern in the cyclopropane ring (Hoffmann, 1970; Allen, 1980). However, this cannot be detected within the limits of experimental error here: the cyclopropane ring is an equilateral triangle (Table 2).

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Structure of 9-Pivaloylfluorene

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Abstract. $\mathrm{C_{18}H_{18}O}$, $M_r = 250\cdot34$, orthorhombic, $P2_12_12_1$, $a = 14\cdot051\ (2)$, $b = 15\cdot769\ (3)$, $c = 6\cdot398\ (4)$ Å, $V = 1417\cdot6\ (8)$ Å^3, $Z = 4$, $D_x = 1\cdot17$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0\cdot66$ cm^{-1}, $F(000) = 536$, $T = 296$ K, $R = 0\cdot046$ for 896 unique reflections. Rotationally hindered 9-pivaloylfluorene (I) was prepared in good yield from the reaction of fluorene with *n*-butyllithium followed by pivaloyl chloride. ^{1}H NMR spectra of all fractions of chromatographed (I) were identical and suggested a single rotamer in solution, the same one shown in the crystal structure: H(9)—C(9)—C(10)—O(1) torsion angle ~180°, the antiperiplanar rotamer, (I*b*).

Introduction. During our initial investigation comparing the reactions of 9-methyl-9-keto-substituted fluorenes with *n*-butyllithium *versus* Grignard reagents (Meyers, Arnold & Wahner, 1975; Arnold, Meyers & Wahner, 1975), previously unreported 9-pivaloylfluorene (I) was prepared but set aside. Darling Molecular Models©, equipped with space-filling H atoms and *p* lobes, suggested that the significant rotational restriction around the C(9)—C(10) bond of (I) might allow it to exist in solution at ambient temperatures as two distinct rotamers, (I*a*) (*sp*) and

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