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148. Structure of 1-*exo*-Phenylbicyclo[2.1.0]pentane-5-carboxylic acid by X-Ray Analysis

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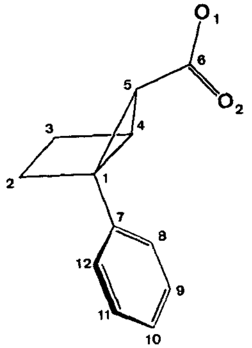
Dedicated to Professor *V. Prelog* on the occasion of his 70th birthday.

(16. III. 76)

Summary. The title compound ($C_{12}H_{12}O_2$) crystallizes in the monoclinic space group $P2_1/c$. The structure was solved by direct methods, and the positions of all the hydrogen atoms were obtained from a difference synthesis. The final R_ω was 0.04. Current MO theories of the interaction of unsaturated groups with small ring systems are consistent with the bond length variations encountered in the present substituted bicyclo[2.1.0]pentane skeleton with respect to the unsubstituted hydrocarbon.

1-Phenylbicyclo[2.1.0]pentane-5-carboxylic acids were prepared by *Schaffner et. al.* in connection with a mechanistic study of the triplet oxa-di-π-methane photorearrangement of β,γ-unsaturated ketones [1]. The synthesis involved $CuSO_4$-catalysed addition of ethyl diazoacetate to 1-phenylcyclobutene. Hydrolysis of the two resulting isomeric ethyl bicyclopentane-carboxylates afforded the acids. The present structure determination was carried out to confirm the *exo* configuration deduced from NMR. data for the isomer of m.p. 131°.



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Experimental part. – The compound was kindly provided by Mrs. *I-M. Tegmo-Larsson.* Colourless, well formed prisms were obtained at room temperature by slow evaporation of a solution in hexane/methylene chloride 10:1. The selected crystal had dimensions 0.18 × 0.19 × 0.24 mm. Lattice parameters and diffracted intensities were measured at room temperature on an automatic four-circle diffractometer (*Philips* PW1100) with Mo$K\alpha$-radiation ($\lambda = 0.71069$ Å) reflected from a graphite monochromator. Crystallographic data are:

$C_{12}H_{12}O_2$ (m.p. 131°). Monoclinic, space group $P2_1/c$, $a = 6.121(3)$, $b = 24.567(8)$, $c = 7.159(3)$ Å, $\beta = 111.83(4)°$; V = 999.34 Å^3; $Z = 4$; $F(000) = 400$; $D_m = 1.267$, $D_x = 1.251$ g cm^{-3}; $\mu = 0.908$ cm^{-1}.

1111 independent reflections were scanned in the θ–2θ mode (scan width 1.0°; scan speed 0.02° s^{-1}) within the limits $3° < \theta < 21°$. The background was measured with a fixed counting time of 5 s on each side of the peaks. Two monitor reflections, measured at average intervals of 40 reflections, showed no signs of crystal degradation. After the usual corrections 900 reflections had $|F_o| > 2\sigma(F_o)$ and were used in the structure analysis.

Structure Analysis and Refinement. – The phase problem was solved by direct methods using the latest version of the X-RAY System [2] computer programs. A straighforward solution was obtained with 138 of the largest normalized structure amplitudes ($E > 1.50$) and 980 triple-phase relationships between them. The resulting E-map revealed the locations of all the non-hydrogen atoms. Positional parameters and anisotropic temperature factors were then refined by full-matrix least-squares analysis. All the H atoms were located from a difference synthesis and included in the structure model. Their positional parameters were simultaneously refined but their thermal parameters were set equal to the average isotropic temperature factor (B = 4.0 Å^2) of the C atoms. The final $R_\omega = (\Sigma\omega\Delta F^2/\Sigma\omega|F_o|^2)^{1/2}$ was 0.04 based on 900 reflections with $\omega = 1/\sigma^2\,(F_o)$; the conventional unweighted R was 0.07.

Discussion of the results. – Molecular dimensions and bond angles not involving H atoms are given in Table 3. The average C–H bond length in the molecule is 1.06(5) Å, the mean external C–C–H bond angle of the phenyl ring is 120 (2)°, and the H–C–H bond angles at atoms C(2) and C(3) and 113° are 108° respectively.

The four-membered ring is planar with standard deviation $\sigma = 0.006$ Å of the atoms from the plane. The three-membered ring is inclined to this plane at an angle 110.1°, which compares with the value 112.7° measured on the unsubstituted parent hydrocarbon [3]. The structure of bicyclo[2.1.0]pentane has been determined by electron diffraction [4] and by a microwave study [3]; unfortunately, the two sets of results are in strong disagreement. As will be shown, the results of the present analysis are consistent with those of the microwave study and indirectly support the arguments presented in [3] regarding the 'long' and 'short' bond length assignment of the electron diffraction structure. The apical atom C(5) and the atoms of the carboxyl group (not including H) define a plane ($\sigma = 0.002$ Å) which is inclined to the three-membered ring at 84.1°. The carbonyl oxygen atom O(2) lies over the three-membered ring but is not equidistant from C(1) and C(4), as expressed by the torsion angles τ[C(1)–C(5)–C(6)–O(2)] = 44.9° and τ[C(4)–C(5)–C(6)–O(2)] = –22.0°. Mutual repulsion between O(2) and C(7) of the phenyl ring at a distance 3.143 Å forces O(2) into close contact (2.71 Å) with H(C4). The steric interaction between the phenyl ring and the carboxyl group is also manifested in the 4° inclination of the C(1)–C(7) bond to the ring plane ($\sigma = 0.006$ Å), to move the latter away from the O atoms. Strong non-bonded interaction also prevails between O(1) and H(C5), only 2.48 Å apart, the latter being in *van der Waals* contact with the *endo* atoms H2(C2) and H1(C3) at 2.47 and 2.44 Å, respectively. The orientation of the phenyl ring to the

Table 1. *Final positional and thermal parameters* ($\times 10^4$) *with standard deviations*. Thermal parameters are given in the form: $\exp[-2\pi^2(a^{*2}U_{11}h^2 + 2a^*b^*U_{12}hk + \cdots)]$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	2659(5)	−196(1)	866(5)	432(25)	376(25)	484(26)	33(21)	222(21)	−139(23)
O(2)	5171(7)	509(1)	1562(5)	508(28)	388(27)	538(28)	99(22)	323(23)	−187(21)
C(1)	1755(8)	1041(2)	3132(8)	288(36)	369(38)	354(37)	4(29)	158(31)	− 59(33)
C(2)	367(9)	1110(2)	4545(8)	429(40)	585(46)	365(38)	95(32)	196(33)	8(33)
C(3)	2541(9)	875(2)	6340(8)	516(43)	615(46)	338(39)	64(34)	199(34)	− 46(32)
C(4)	3828(8)	806(2)	4892(8)	283(36)	554(43)	333(37)	80(32)	66(31)	− 32(34)
C(5)	2405(9)	431(2)	3191(7)	406(37)	272(37)	324(37)	12(30)	181(32)	− 24(30)
C(6)	3585(10)	267(2)	1810(8)	437(42)	295(41)	266(38)	157(35)	29(34)	− 19(33)
C(7)	1531(10)	1420(2)	1478(8)	471(45)	254(37)	305(40)	28(34)	200(36)	− 3(31)
C(8)	3434(9)	1706(2)	1397(8)	495(46)	410(41)	473([illegible])	52(36)	222(37)	− 22(34)
C(9)	3067(12)	2089(2)	− 171(11)	832(63)	387(46)	787(58)	−148(42)	562(51)	− 91(41)
C(10)	840(15)	2179(2)	−1564(9)	1095(72)	390(47)	407(47)	197(47)	315(50)	99(36)
C(11)	−1067(12)	1886(3)	−1482(9)	687(56)	513(48)	512(49)	3(42)	122(40)	− 54(41)
C(12)	− 694(11)	1503(2)	48(9)	663(52)	254(39)	382(40)	36(35)	155(38)	79(32)

Table 2. *Observed positional parameters of the hydrogen atoms* (× 10^4). B was set equal to 4.0 ($Å^2$) which is the average isotropic thermal parameter of the carbon atoms.

Atom	x	y	z
H1(C2)	11	1550	4724
H2(C2)	−1174	875	3975
H1(C3)	2214	491	6920
H2(C3)	3078	1141	7488
H(C4)	5664	870	5272
H(C5)	1342	140	3534
H(C8)	5095	1644	2487
H(C9)	4359	2366	− 159
H(C10)	513	2427	−2702
H(C11)	−2862	1935	−2761
H(C12)	−2193	1266	111
H(O1)	3889	−359	50

Table 3. *Molecular parameters derived from coordinates of Tables 1 and 2*

Bond distances (Å). Standard deviations (× 10^3) are in parentheses.

C(1)—C(2)	1.554(9)	C(6)—O(1)	1.338(6)
C(1)—C(4)	1.528(6)	C(6)—O(2)	1.207(8)
C(1)—C(5)	1.549(7)	C(7)—C(8)	1.381(9)
C(1)—C(7)	1.472(8)	C(7)—C(12)	1.379(7)
C(2)—C(3)	1.573(7)	C(8)—C(9)	1.418(9)
C(3)—C(4)	1.528(9)	C(9)—C(10)	1.373(9)
C(4)—C(5)	1.517(7)	C(10)—C(11)	1.391(11)
C(5)—C(6)	1.481(9)	C(11)—C(12)	1.398(9)

Bond angles (°). The average standard deviation is 0.5°.

C(2)—C(1)—C(4)	89.5	C(4)—C(5)—C(6)	115.1
C(2)—C(1)—C(5)	106.6	C(5)—C(6)—O(1)	110.3
C(2)—C(1)—C(7)	123.0	C(5)—C(6)—O(2)	125.8
C(4)—C(1)—C(5)	59.1	O(1)—C(6)—O(2)	123.9
C(4)—C(1)—C(7)	134.5	C(1)—C(7)—C(8)	122.0
C(5)—C(1)—C(7)	125.5	C(1)—C(7)—C(12)	117.4
C(1)—C(2)—C(3)	89.5	C(8)—C(7)—C(12)	120.5
C(2)—C(3)—C(4)	88.8	C(7)—C(8)—C(9)	119.1
C(1)—C(4)—C(5)	61.1	C(8)—C(9)—C(10)	120.1
C(3)—C(4)—C(1)	92.1	C(9)—C(10)—C(11)	120.5
C(3)—C(4)—C(5)	109.0	C(10)—C(11)—C(12)	119.2
C(1)—C(5)—C(6)	115.4	C(11)—C(12)—C(7)	120.6
C(4)—C(5)—C(1)	59.8		

bicyclic skeleton is such that C(7)–C(8) is *synplanar* (τ = 8.5°) with C(1)–C(4), to give a H(C8) ... O(2) distance of 2.87 Å. There are no other intramolecular contacts between the phenyl hydrogen atoms and other atoms separated by more than three bonds.

The electronic structure of cyclopropane and cyclobutane is a subject of considerable interest, and *Hoffmann* [5] has discussed models based on *Walsh* orbitals and the effects of unsaturated substituents on equilibrium geometries. In a cyclopropane ring substituted by a π-electron acceptor, the ring bond opposite to the atom bearing the substituent is expected to be shortened, whereas the adjacent bonds should be lengthened. This has been demonstrated in several crystal structures[1]. The bond lengths in unsubstituted bicyclo[2.1.0]pentane (C_s symmetry) are [3]: C(1)–C(2) = 1.528; C(1)–C(4) = 1.536; C(1)–C(5) = 1.507 and C(2)–C(3) = 1.565 Å. According to our results (Table 3), substitution by a C_6H_5 and a COOH group induces significant bond lengths variations and, as a whole, increases the *average* C–C bond distance from 1.517 to 1.531 Å in the three-membered ring, and from 1.539 to 1.546 Å in the four-membered ring. This might be the consequence of certain amount of electron transfer to the adjacent unsaturated groups. Delocalization on the COOH group should shorten C(1)–C(4) bond and lengthen C(1)–C(5) and C(4)–C(5). A lower acceptor strength, paralleled by a smaller effect, can be expected for the C_6H_5 group; this should lengthen C(4)–C(5). The lengthening effect of both substituents adds at the C(1)–C(5) bond, which, correspondingly, is 0.042 Å longer than in the parent compound and the longest in the three-membered ring of **1**. The weakening effect of C_6H_5 on the

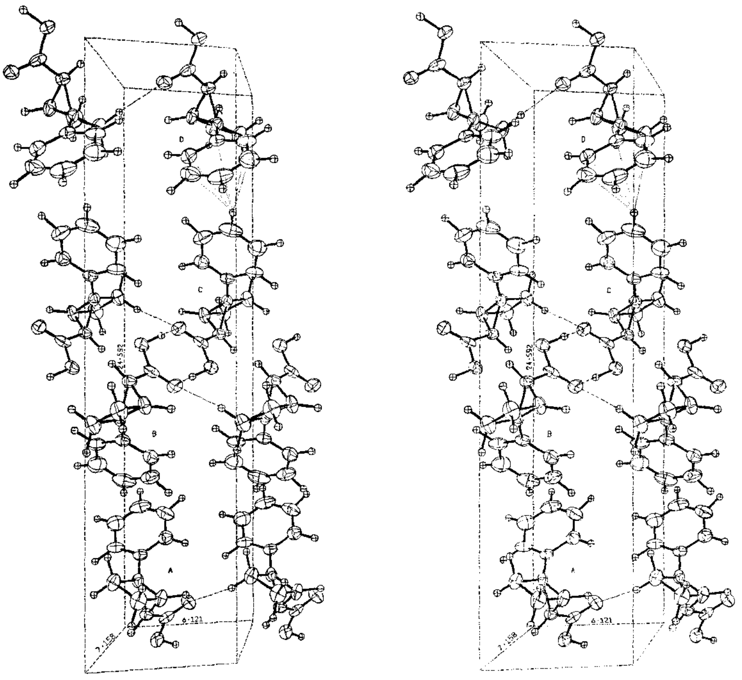

Fig. 1. *Stereoscopic view of the molecular packing showing hydrogen-bonds and short non-bonded contacts.* For clarity, several molecules are represented in addition to the unit-cell contents. The origin and the basic molecule (A; x, y, z) are in the rear, lower left corner.

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[1] See [6] [7] and references therein.

adjacent C(1)–C(4) bond does not cancel the opposite influence of COOH, and a net shortening of the bond ensues, in spite of the additional strain resulting from fusion with the cyclobutane ring. There is too little experimental evidence to conclude whether the lengthening of C(1)–C(2) is also due to conjugation with the phenyl ring. In the planar, centrosymmetric 1,2,3,4-tetraphenylcyclobutane [8] the ring bond length (1.57 Å) is also longer than the 'normal' bond length (1.548 Å) of puckered cyclobutane [9], but the effects of steric repulsion between adjacent phenyl rings in the tetrasubstituted molecule would have to be allowed for. The C(1)–C(7) bond is significantly shorter than the value 1.50–1.53 Å expected for a normal C(sp^2)–C(sp^3) bond [10], which might well be a consequence of the remarkable bond environment.

The stereoscopic view (Fig. 1) shows the shortest intermolecular distances. Hydrogen bonding between carboxyl groups leads to the characteristic formation of centrosymmetric dimers (e.g. molecules B and C, Fig. 1). The O(2) ... H–O(1) distance is 2.666 Å, and the H atom subtends an angle of 162°. Molecules related by the unit translation along the *a* axis are in close contact through atoms C(2)–H2 ... O(2)′ at distance C(2) ... O(2)′ of 3.432 Å and H2 ... O(2) of 2.43 Å. For adjacent molecules related by the glide plane (*e.g.* C and D, Fig. 1), the *para* H atom of one phenyl ring lies above the centre of the other phenyl ring, equidistant from the six C atoms (average distance H ... C (ring) = 3.01 (1) Å).

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