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## Substituent Effects on the Bicyclo[1.1.0]butane System. Structures of Bicyclo[1.1.0]butane Derivatives Substituted by Carbonyl and Carboxylate Groups

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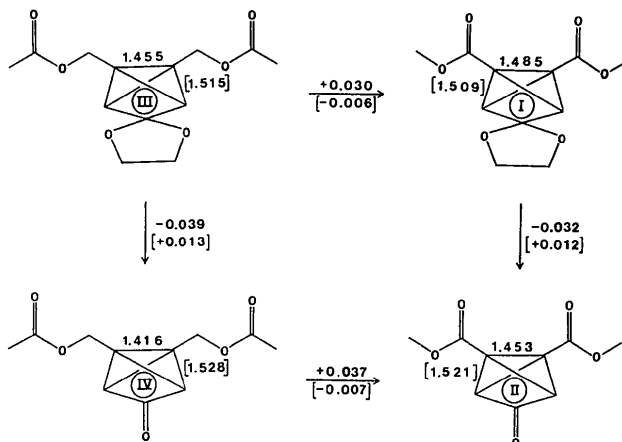
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**Abstract.** Structures of two bicyclo[1.1.0]butane derivatives substituted by methoxycarbonyl groups on the bridgehead carbon atoms C(1) and C(2) and linked on C(3) and C(4) by a ketal group (I) or by a carbonyl group (II). (I):  $C_{11}H_{12}O_6$ ,  $M_r = 240.21$ , monoclinic,  $P2_1/c$ ,  $a = 11.546$  (1),  $b = 12.141$  (2),  $c = 8.319$  (2) Å,  $\beta = 79.29$  (1)°,  $V = 1145.8$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.39$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.11$  mm<sup>-1</sup>,  $F(000) = 504$ ,  $T = 295$  K,  $R = 0.043$  for 1782 unique observed reflections [ $I > 3\sigma(I)$ ]. (II):  $C_9H_8O_5$ ,  $M_r = 196.16$ , triclinic,  $P\bar{1}$ ,  $a = 5.726$  (1),  $b = 7.033$  (1),  $c = 10.734$  (1) Å,  $\alpha = 88.48$  (1),  $\beta = 88.18$  (1),  $\gamma = 84.76$  (1)°,  $V = 430.1$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.51$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.12$  mm<sup>-1</sup>,  $F(000) = 204$ ,  $T = 295$  K,  $R = 0.037$  for 2078 unique observed reflections [ $I > 3\sigma(I)$ ]. The methoxycarbonyl groups at the bridgehead carbon atoms C(1) and C(2) of (I) give rise to a lengthening of the central bond [1.485 (2) Å] by 0.030 Å compared to the corresponding compound (III) which lacks  $\pi$ -accepting substituents. The corresponding central bond [1.453 (2) Å] of (II) is shortened compared with (I) by the effect of the CO group linking C(2) and C(3). By the same effect

the remaining four bonds of the bicyclobutane system of (II) are lengthened by 0.012 Å [(I) 1.509 (3) Å; (II) 1.521 (5) Å].

**Introduction.** The central bond in bicyclo[1.1.0]butane derivatives is very sensitive to electronic effects of substituents and to changes of the dihedral angle between both three-membered rings (Irngartinger & Lukas, 1979; Allen, 1984). To obtain further information about the substituent effects, we investigated the structure of bicyclo[1.1.0]butane derivatives with equal dihedral angles. This angle is fixed by linking C(3) and C(4) (Fig. 1) with one carbon C(5) in order to find the pure substituent effects on the central bond without interference by steric influences. Our aim was to discover the effect of  $\pi$ -acceptor groups (e.g. the carbonyl group) on the bond lengths of bicyclo[1.1.0]butane, if the groups are substituted in different positions, and to determine their combined influence in polysubstituted systems. Therefore, we determined the structures of dimethyl spiro(1,3-dioxolane-2,3'-tricyclo[2.1.0.0<sup>2,5</sup>]pentane)-1',5'-dicarboxylate (I) and dimethyl 3-oxotricyclo[2.1.0.0<sup>2,5</sup>]pentanedicarboxylate

(II) and compared them with the structures of (III) (Irngartinger, Goldmann, Schappert, Garner, Go & Dowd, 1985) and (IV) (Dowd, Garner, Schappert, Irngartinger & Goldmann, 1982).



**Experimental.** Colourless crystals of (I) and (II) ( $0.6 \times 0.3 \times 0.25$  and  $0.4 \times 0.3 \times 0.15$  mm) crystallized from diethyl ether/pentane and dichloromethane/hexane, respectively. Data measured on a CAD-4 diffractometer (Enraf-Nonius) at 295 K.  $\omega$ - $2\theta$  scan method, 2568 (I) and 2078 (II) unique reflections up to  $(\sin\theta)/\lambda = 0.66 \text{ \AA}^{-1}$ . The structures have been solved by direct methods [*MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982)] and refined by full-matrix least squares on  $F^2$  with anisotropic thermal parameters for C and O atoms and isotropic thermal parameters for H atoms.  $wR = 0.057$  (I),  $0.058$  (II),  $w = 4F^2/[\sigma^2/(F^2) + (0.03F^2)^2]$ ,  $S = 2.62$  (I),  $2.81$  (II),  $(\Delta/\sigma)_{\max} < 0.02$ , largest peak  $0.3$  (I),  $0.2$  (II)  $e \text{ \AA}^{-3}$ . Scattering factors from *International Tables for X-ray Crystallography* (1974); *SDP* programs (Frenz, 1982) used on a PDP 11/44.

**Discussion.** The final atomic parameters for (I) and (II) are listed in Tables 1 and 2.\* Bond lengths are given in Figs. 1 and 2; bond angles are listed in Tables 3 and 4.

The dihedral angles between the three-membered rings in the bicyclobutanes (I) to (IV) have the same order of magnitude:  $98.7$  (2),  $98.9$  (2),  $96.8$  (2),  $95.7$  (2) $^\circ$ . The central bond of compound (III), not influenced by  $\pi$  acceptors, has a distance of  $1.455$  (3)  $\text{\AA}$ . The  $\pi$ -accepting carboxylate groups on the bridgehead carbon atoms C(1) and C(2) of (I) give rise to a lengthening of the central bond C(1)–C(2) to

\* Lists of H-atom positions and the corresponding bond distances and angles, anisotropic thermal parameters of non-H atoms, and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44917 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for (I)

$U_{eq}$  is one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
O(1)	0.2983 (1)	-0.0696 (1)	0.4939 (1)	58 (1)
O(2)	0.1383 (1)	-0.1271 (1)	0.3980 (2)	77 (1)
O(3)	0.4854 (1)	0.1646 (1)	0.0955 (2)	90 (1)
O(4)	0.3516 (1)	0.2739 (1)	0.2446 (2)	67 (1)
O(5)	0.0823 (1)	0.1845 (1)	0.0758 (2)	67 (1)
O(6)	0.1533 (1)	0.0411 (1)	-0.0797 (1)	54 (1)
C(1)	0.3083 (1)	0.0902 (1)	0.2372 (2)	45 (1)
C(2)	0.2012 (1)	0.0545 (1)	0.1765 (2)	45 (1)
C(3)	0.1950 (1)	0.0714 (1)	0.3572 (2)	45 (1)
C(4)	0.2928 (2)	-0.0300 (1)	0.1989 (2)	49 (1)
C(5)	0.2287 (1)	-0.0490 (1)	0.3767 (2)	50 (1)
C(6)	0.2644 (2)	-0.1714 (2)	0.5702 (3)	84 (1)
C(7)	0.1502 (2)	-0.1995 (2)	0.5250 (3)	72 (1)
C(8)	0.3919 (1)	0.1776 (1)	0.1835 (2)	51 (1)
C(9)	0.4254 (2)	0.3697 (2)	0.1974 (3)	84 (2)
C(10)	0.1398 (1)	0.1021 (1)	0.0549 (2)	44 (1)
C(11)	0.0941 (2)	0.0821 (2)	-0.2068 (2)	65 (1)

Table 2. Atomic coordinates and thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for (II)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
O(1)	0.6023 (2)	0.1799 (1)	0.9217 (1)	47 (1)
O(2)	0.1664 (2)	0.1718 (2)	0.5045 (1)	47 (1)
O(3)	-0.1246 (2)	0.2353 (1)	0.6465 (1)	37 (1)
O(4)	0.2315 (2)	-0.4165 (1)	0.7516 (1)	50 (1)
O(5)	-0.0681 (2)	-0.2538 (1)	0.8542 (1)	40 (1)
C(1)	0.2207 (2)	0.0867 (2)	0.7164 (1)	31 (1)
C(2)	0.2425 (2)	-0.0887 (2)	0.7914 (1)	32 (1)
C(3)	0.4657 (2)	-0.0072 (2)	0.7418 (1)	34 (1)
C(4)	0.2013 (2)	0.0992 (2)	0.8578 (1)	32 (1)
C(5)	0.4651 (2)	0.1105 (2)	0.8600 (1)	34 (1)
C(6)	0.0895 (2)	0.1668 (2)	0.6094 (1)	31 (1)
C(7)	-0.2739 (3)	0.3245 (2)	0.5517 (2)	49 (1)
C(8)	0.1396 (2)	-0.2725 (2)	0.7953 (1)	32 (1)
C(9)	-0.1964 (3)	-0.4219 (2)	0.8638 (2)	51 (1)

Table 3. Bond angles ( $^\circ$ ) for (I)

C(5)–O(1)–C(6)	108.9 (2)	C(2)–C(3)–C(5)	90.6 (1)
C(5)–O(2)–C(7)	110.2 (2)	C(2)–C(4)–C(1)	58.9 (1)
C(8)–O(4)–C(9)	117.2 (1)	C(1)–C(4)–C(5)	89.8 (1)
C(10)–O(6)–C(11)	115.3 (1)	C(2)–C(4)–C(5)	89.8 (1)
C(3)–C(1)–C(2)	60.4 (1)	O(1)–C(5)–O(2)	107.6 (1)
C(4)–C(1)–C(2)	60.5 (1)	O(1)–C(5)–C(3)	115.8 (1)
C(2)–C(1)–C(8)	131.2 (2)	O(1)–C(5)–C(4)	117.4 (1)
C(3)–C(1)–C(4)	82.6 (1)	O(2)–C(5)–C(3)	117.6 (1)
C(3)–C(1)–C(8)	139.6 (2)	O(2)–C(5)–C(4)	115.9 (1)
C(4)–C(1)–C(8)	137.8 (1)	C(3)–C(5)–C(4)	80.9 (1)
C(1)–C(2)–C(3)	60.6 (1)	O(1)–C(6)–C(7)	105.9 (2)
C(1)–C(2)–C(4)	60.6 (1)	O(2)–C(7)–C(6)	105.3 (2)
C(1)–C(2)–C(10)	131.5 (1)	O(3)–C(8)–O(4)	124.3 (2)
C(3)–C(2)–C(4)	82.7 (1)	O(3)–C(8)–C(1)	124.5 (2)
C(3)–C(2)–C(10)	134.4 (1)	O(4)–C(8)–C(1)	111.2 (1)
C(4)–C(2)–C(10)	142.8 (1)	O(5)–C(10)–O(6)	124.4 (2)
C(2)–C(3)–C(1)	59.0 (1)	O(5)–C(10)–C(2)	124.0 (2)
C(1)–C(3)–C(5)	90.5 (1)	O(6)–C(10)–C(2)	111.6 (1)

$1.485$  (2)  $\text{\AA}$ . The additional carbonyl group on C(3) and C(4) in (II) has the opposite effect and shortens the central bond C(1)–C(2) by the same amount to  $1.453$  (2)  $\text{\AA}$ . Compared to (III) the substituent effects on the central bond of (II) neutralize each other. In (IV) only the shortening property of the carbonyl group is

Table 4. Bond angles (°) for (II)

C(6)–O(3)–C(7)	116.6 (1)	C(1)–C(3)–C(5)	88.6 (1)
C(8)–O(5)–C(9)	116.8 (1)	C(2)–C(3)–C(5)	88.8 (1)
C(3)–C(1)–C(2)	61.5 (1)	C(2)–C(4)–C(1)	57.2 (1)
C(4)–C(1)–C(2)	61.1 (1)	C(1)–C(4)–C(5)	89.1 (1)
C(2)–C(1)–C(6)	138.6 (1)	C(2)–C(4)–C(5)	89.6 (1)
C(3)–C(1)–C(4)	83.6 (1)	O(1)–C(5)–C(3)	138.4 (1)
C(3)–C(1)–C(6)	137.9 (1)	O(1)–C(5)–C(4)	138.2 (1)
C(4)–C(1)–C(6)	137.1 (1)	C(3)–C(5)–C(4)	83.4 (1)
C(1)–C(2)–C(3)	61.6 (1)	O(2)–C(6)–O(3)	125.4 (1)
C(1)–C(2)–C(4)	61.7 (1)	O(2)–C(6)–C(1)	124.6 (1)
C(1)–C(2)–C(8)	137.1 (1)	O(3)–C(6)–C(1)	110.0 (1)
C(3)–C(2)–C(4)	83.9 (1)	O(4)–C(8)–O(5)	125.8 (1)
C(3)–C(2)–C(8)	138.2 (1)	O(4)–C(8)–C(2)	124.5 (1)
C(4)–C(2)–C(8)	136.8 (1)	O(5)–C(8)–C(2)	109.7 (1)
C(2)–C(3)–C(1)	56.9 (1)		

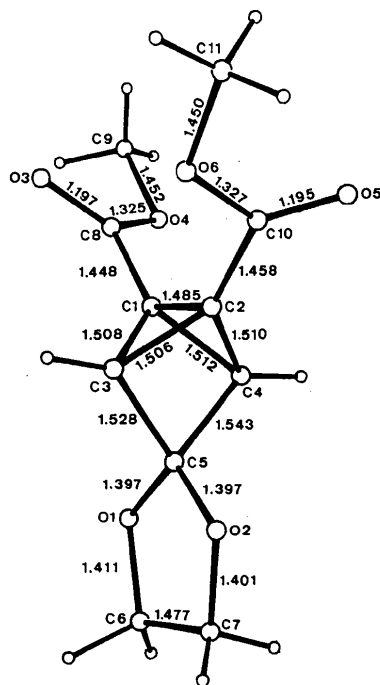


Fig. 1. Bond lengths (Å) for (I). Standard deviations 0.002–0.003 Å.

effective (scheme). The CO groups of both carboxylate substituents in (I) and in (II) have an optimal orientation for interactions with the bicyclobutane moiety. The angles between the C–C=O planes and the planes bisecting the dihedral angles of both three-membered rings [C(1), C(2), C(5), C(8), C(10) for (I) and C(1), C(2), C(5), C(6), C(8) for (II)] are close to 90°: 78.7 (3) [C(8), (I)], 77.0 (3) [C(10), (I)], 80.8 (2) [C(6), (II)] and 81.9 (2)° [C(8), (II)]. Relative to this bisecting plane the carboxylate groups are *trans* (I) or *cis* (II) oriented (Figs. 1 and 2). Compared with the effect on the central bond, the substituent effects on the remaining four bonds C(1)–C(3), C(1)–C(4), C(2)–C(3) and C(2)–C(4) of the bicyclobutane system tend in the opposite direction and are smaller: one fifth for the COOR groups [shortening (III)→(I); (IV)→(II)] and

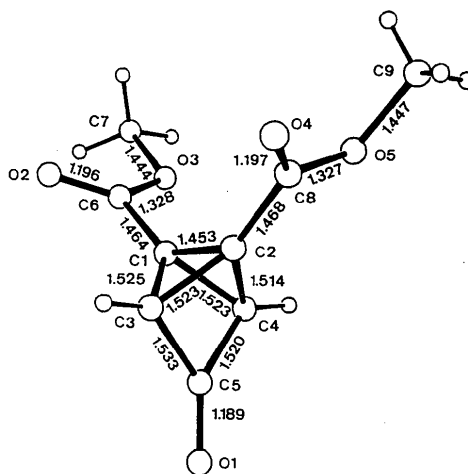


Fig. 2. Bond lengths (Å) for (II). Standard deviations 0.002 Å.

one third for the C(5)=O(1) group [lengthening (I)→(II), (III)→(IV); scheme and Figs. 1 and 2; average values given in square brackets]. On the average the substituent effects of two carboxylate groups on the bridgehead carbon atoms or of a CO group linking C(3) and C(4) of the bicyclobutane system change the central bond by 0.035 (4) Å and the remaining four bonds by 0.010 (4) Å. The angles on the bridgehead carbon atoms between the central bond and the exocyclic bond are opened up by the influence of the C(5)–O(1) group [131.4 (2)° for (I), 137.9 (11)° for (II); Tables 3 and 4] (Irngartinger, Jahn, Rodewald, Paik & Dowd, 1987).

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