

Fig. 2. Stereoprojection (Johnson, 1976) of (1) from the *ac* plane to *b/2* down the *b* axis. Some molecules have been omitted for clarity, see text.

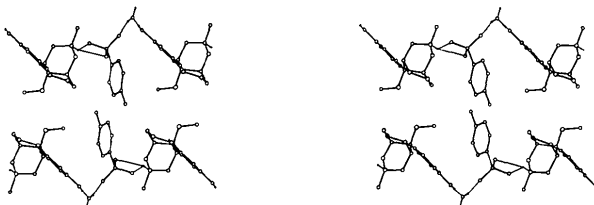


Fig. 3. Stereoprojection (Johnson, 1976) of (1) from *b/4* to  $-b/4$  down the *c* axis. Some molecules have been omitted for clarity, see text.

unshared electron pair on N. It is clear that in the chair-boat conformation of (1) the C(9) substituents would invoke even more severe non-bonded bowsprit repulsions than those encountered in the chair-boat conformation of bicyclo[3.3.1]nonane. Accordingly, (1) conforms to the definition of an effectively rigid chair-chair conformation (Eliel, Allinger, Angyal & Morrison, 1965).

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## Methyl 8-Oxotricyclo[5.4.0.0<sup>2,6</sup>]undecane-1-carboxylate, C<sub>13</sub>H<sub>18</sub>O<sub>3</sub>

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**Abstract.**  $M_r = 222.3$ , monoclinic, *Cc*.  $a = 8.399(3)$ ,  $b = 16.366(3)$ ,  $c = 9.310(3)$  Å,  $\beta = 108.19(2)^\circ$ ,  $V = 1215.8$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.21$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha_1) = 0.70926$  Å,  $\mu = 0.79$  cm<sup>-1</sup>,  $F(000) = 480$ ,  $T = 294$  K. Final  $R = 0.047$  for 891 observed reflections. The five- and six-membered rings are mutually *trans*-disposed

about the central four-membered ring. One of the atoms of the six-membered ring is disordered over two sites (0.75:0.25) leading to twist-boat and twist-chair conformations for this ring; the four-membered ring is puckered [torsion angles  $\pm 9.4(3)^\circ$ ] and the five-membered ring has an *endo*-envelope conformation.

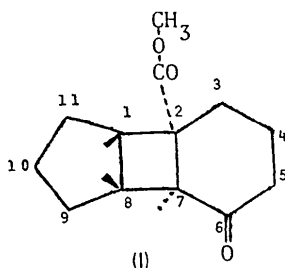
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### References

- BHATTACHARJEE, S. K. & CHACKO, K. K. (1979). *Tetrahedron*, **35**, 1999–2007.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
- COCHRAN, T. G. (1974). *J. Med. Chem.* **17**, 987–989.
- DECLERCQ, J.-P., GERMAIN, G. & WOOLFSON, M. M. (1975). *Acta Cryst.* **A31**, 367–372.
- DOBLER, M. & DUNITZ, J. D. (1964). *Helv. Chim. Acta.* **47**, 695–704.
- ELIEL, E. L., ALLINGER, N. L., ANGYAL, S. J. & MORRISON, G. A. (1965). *Conformational Analysis*, ch. 2, pp. 36–128. New York: Interscience.
- FRIES, D. S., DODGE, R. P., HOPE, H. & PORTOGHESE, P. S. (1982). *J. Med. Chem.* **25**, 9–12.
- FROIMOWITZ, M. (1982). *J. Med. Chem.* **25**, 1127–1133.
- FROIMOWITZ, M., SALVA, P., HITE, G., GIANUTSOS, G., SUZDAK, P. & HEYMAN, R. (1984). *J. Comput. Chem.* In the press.
- International Tables for X-ray Crystallography* (1974). Vol. IV, Table 2.2B, pp. 99–102. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- LEWIS, T. W., PAUL, I. C. & CURTIN, D. Y. (1980). *Acta Cryst.* **B36**, 70–77.
- MASTRYUKOV, V. S., POPIK, M. V., DOROFEEVA, O. V., GOLUBINSKII, A. V., VILKOV, L. V., BELIKOVA, N. A. & ALLINGER, N. L. (1979). *Tetrahedron Lett.* **45**, 4339–4342.
- NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- OHKI, E., OIDA, S., OHASHI, Y., TAKAGI, H. & IWAI, I. (1970). *Chem. Pharm. Bull.* **18**, 2050–2057.
- PORTOGHESE, P. S. (1965). *J. Med. Chem.* **8**, 609–616.
- PORTOGHESE, P. S. (1978). *Acc. Chem. Res.* **11**, 21–28.
- SMITH-VERDIER, P., FLORENCIO, F. & GARCÍA-BLANCO, S. (1983). *Acta Cryst.* **C39**, 101–103.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. W. & HALL, S. R. (1972). The *XRAY* system. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- TECLE, H. & HITE, G. (1976). Proc. 38th Annu. Meet., Comm. on Problems of Drug Dependence, National Academy of Sciences, USA, p. 464.

**Introduction.** The analysis was undertaken to establish unequivocally the stereochemistry at the ring junctions and to determine the ring conformations in the solid state of the title compound (1) shown below (this formula also shows the numbering scheme used in the analysis). These data could not be readily determined from spectroscopic studies of (1) and its derivatives (Lange, 1983).



**Experimental.** Colourless crystals from petroleum-ether, 0.30 × 0.20 × 0.20 mm, CAD-4 diffractometer, graphite-monochromatized Mo K $\alpha$  radiation, 25 reflections with  $\theta$  in the range  $10 < \theta < 12^\circ$  used for determining lattice constants and orientation matrix; for data collection  $2 < \theta < 25^\circ$  ( $h = -9$  to  $+9$ ,  $k = 0$  to  $19$ ,  $l = 0$  to  $11$ ),  $\omega - 2\theta$  scans,  $\omega$ -scan width  $(0.80 + 0.35 \tan \theta)^\circ$ ; intensities of three standard reflections measured every 100 min of exposure time showed a 9% decay over the period of the data collection and this was compensated for by appropriate scaling; Lp corrections, 1065 unique reflections, 891 (83.7%) with  $I > 3\sigma(I)$ , where  $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$ ,  $S =$  scan count and  $B =$  time-averaged background count; absorption corrections not considered necessary. The systematic absences ( $hkl$  absent if  $h+k = 2n+1$ ,  $h0l$  absent if  $l = 2n+1$ ) allow the space group to be  $C2/c$  or  $Cc$ . No twofold or inversion symmetry is possible for (1); with  $Z = 4$ ,  $C2/c$  does require either twofold or inversion symmetry and was therefore discounted. The choice of  $Cc$  was confirmed by the  $E$  statistics and the successful solution of the structure and refinement. Initial phases were determined with the *MULTAN80* (Main *et al.*, 1980) direct-methods segment of the *NRC Crystal Structure Package* (Gabe, Larson, Wang & Lee, 1981). Difference maps at intermediate stages in the analysis showed that C(4) is disordered over two sites with occupancy factors 0.75:0.25 (from peak densities). Refinement on  $F$ , initially by full-matrix isotropic least-squares calculations, and finally by block-diagonal calculations with anisotropic thermal parameters for non-H atoms. H atoms (all visible in difference maps except for those of the minor conformer) were included in the last round of calculations at idealized positions (C-H = 1.08 Å) but not refined. The H atoms of the methyl group are disordered over two orientations with equal occupancy. Final  $R = 0.047$ ,  $R_w = 0.041$  for the 891 observed reflections,  $R = 0.055$  for all data

Table 1. Final fractional coordinates and isotropic thermal parameters with e.s.d.'s in parentheses

$$\text{Mean } B_{\text{iso}}(\text{\AA}^2) = \frac{8}{3}\pi^2(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$B_{\text{iso}}$
O(1)	0.0	0.7144 (1)	0.0	7.6 (2)
O(2)	-0.0370 (4)	0.7899 (2)	-0.2049 (3)	7.7 (2)
O(3)	-0.4454 (4)	0.9838 (2)	-0.2718 (4)	7.5 (2)
C(1)	-0.0578 (6)	0.8818 (2)	0.1222 (4)	6.0 (3)
C(2)	-0.1619 (5)	0.8326 (2)	-0.0178 (4)	5.1 (2)
C(3)	-0.3086 (7)	0.7840 (2)	0.0066 (7)	9.4 (4)
C(4A)	-0.4577 (9)	0.8342 (4)	0.0036 (8)	7.6 (3)
C(4B)	-0.4490 (19)	0.7893 (9)	-0.0829 (21)	6.0 (11)
C(5)	-0.5263 (5)	0.8817 (3)	-0.1296 (5)	7.4 (3)
C(6)	-0.4023 (5)	0.9305 (2)	-0.1782 (4)	5.2 (2)
C(7)	-0.2189 (4)	0.9140 (2)	-0.1023 (4)	4.3 (2)
C(8)	-0.1404 (5)	0.9628 (2)	0.0469 (4)	5.2 (2)
C(9)	-0.0033 (6)	1.0217 (2)	0.0434 (5)	6.1 (2)
C(10)	0.1416 (5)	0.9652 (3)	0.0416 (6)	8.0 (4)
C(11)	0.1286 (6)	0.8953 (3)	0.1463 (5)	7.7 (3)
C(12)	-0.0609 (5)	0.7787 (2)	-0.0868 (4)	5.0 (2)
C(13)	0.1005 (7)	0.6578 (3)	-0.0526 (5)	8.9 (4)

Table 2. Molecular dimensions

(a) Bond lengths (Å)

O(1)-C(12)	1.328 (4)	C(3)-C(4A)	1.491 (8)
O(1)-C(13)	1.439 (5)	C(3)-C(4B)	1.216 (17)
O(2)-C(12)	1.191 (5)	C(4A)-C(5)	1.423 (8)
O(3)-C(6)	1.206 (5)	C(4B)-C(5)	1.648 (16)
C(1)-C(2)	1.550 (6)	C(5)-C(6)	1.491 (6)
C(1)-C(8)	1.557 (5)	C(6)-C(7)	1.505 (5)
C(1)-C(11)	1.527 (7)	C(7)-C(8)	1.558 (5)
C(2)-C(3)	1.541 (6)	C(8)-C(9)	1.510 (6)
C(2)-C(7)	1.545 (5)	C(9)-C(10)	1.533 (6)
C(2)-C(12)	1.501 (5)	C(10)-C(11)	1.529 (8)

(b) Bond angles ( $^\circ$ )

C(12)-O(1)-C(13)	117.3 (2)	O(3)-C(6)-C(5)	121.8 (4)
C(2)-C(1)-C(8)	90.5 (3)	O(3)-C(6)-C(7)	120.1 (3)
C(2)-C(1)-C(11)	118.9 (3)	C(5)-C(6)-C(7)	118.1 (3)
C(8)-C(1)-C(11)	103.7 (3)	C(2)-C(7)-C(6)	120.2 (3)
C(1)-C(2)-C(3)	114.3 (4)	C(2)-C(7)-C(8)	90.6 (3)
C(1)-C(2)-C(7)	89.1 (3)	C(6)-C(7)-C(8)	114.4 (3)
C(1)-C(2)-C(12)	114.8 (3)	C(1)-C(8)-C(7)	88.3 (3)
C(3)-C(2)-C(7)	112.6 (3)	C(1)-C(8)-C(9)	108.5 (3)
C(3)-C(2)-C(12)	110.1 (3)	C(7)-C(8)-C(9)	114.9 (3)
C(7)-C(2)-C(12)	114.6 (3)	C(8)-C(9)-C(10)	103.2 (3)
C(2)-C(3)-C(4A)	114.7 (4)	C(9)-C(10)-C(11)	103.3 (4)
C(2)-C(3)-C(4B)	120.8 (9)	C(1)-C(11)-C(10)	106.8 (3)
C(3)-C(4A)-C(5)	115.2 (5)	O(1)-C(12)-O(2)	122.7 (3)
C(3)-C(4B)-C(5)	117.6 (1.1)	O(1)-C(12)-C(2)	111.5 (3)
C(4A)-C(5)-C(6)	115.2 (4)	O(2)-C(12)-C(2)	125.8 (3)
C(4B)-C(5)-C(6)	108.5 (6)		

surveyed (1065),  $w = 1/\sigma^2(F)$ , final difference map was essentially featureless (maxima  $< 0.11 \text{ e \AA}^{-3}$ ), max. coordinate shift/e.s.d. 0.12 for the  $z$  coordinate of C(4B), mean coordinate shift/e.s.d. 0.06, max. temperature shift/e.s.d. 0.10 for the  $U_{33}$  parameter of C(4A), mean temperature shift/e.s.d. 0.03; atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). Other computer programs used included *XANADU* (Roberts & Sheldrick, 1975) and *ORTEPII* (Johnson, 1976).

**Discussion.** Final atomic parameters are in Table 1. Table 2 contains details of molecular dimensions.\*

The analysis establishes the nature of the ring fusions of the title compound to be as shown in (1), with the five- and six-membered rings mutually *trans*. Fig. 1 shows the molecular conformation and numbering scheme. The disorder at C(4) [atoms C(4A) and C(4B) in Fig. 1] does not appear to have any major effect on the remainder of the molecule [although some small disorder at C(3) and C(5) cannot be ruled out]; what it does show is that the six-membered ring is conformationally labile, and this undoubtedly results in the difficulties experienced in interpreting the NMR spectra of the material in solution (Lange, 1983). The major conformer has the six-membered ring in a deformed boat conformation with C(4A)  $-0.561(7)$  and C(7)  $-0.184(5)$  Å from the C(2), C(3), C(5), C(6) plane (mean-plane data have been deposited†); in the minor conformer a deformed chair is found, with C(4B)  $+0.52(2)$  Å from the same four-atom plane. The carbonyl group, C(6)=O(3), is oriented with respect to the ring system so that the torsion angle O(3)—C(6)—C(7)—C(8) is  $91.1(3)^\circ$ , a conformation not at all obvious from a study of molecular models which might lead one to anticipate a value around  $135^\circ$ .

The bond lengths at C(4A) [ $1.491(8)$  and  $1.423(8)$  Å] are shorter than anticipated, and those at C(4B) [ $1.22(2)$  and  $1.65(2)$  Å] are anomalous.

\* Lists of structure amplitudes, anisotropic thermal parameters, torsion angles, mean-plane data, and the calculated H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39147 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† See previous footnote.

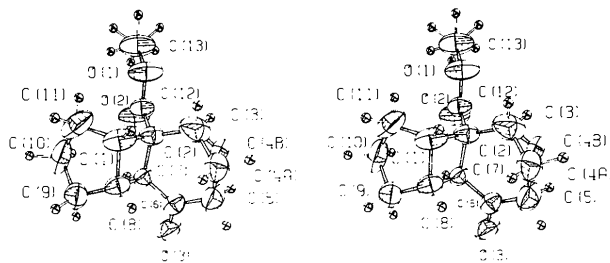


Fig. 1. A stereoview of the molecule and the crystallographic numbering scheme. The disordered atom C(4) is shown as C(4A) (major conformer) and as C(4B) (minor conformer). The three H atoms of the methyl carbon C(13) are disordered equally over two sites.

Various attempts were made to improve the C(4A) and C(4B) positions *via* difference maps and refinement, but to no avail. It is possible that C(4) is disordered over several sites between the two extreme boat and chair conformations; there is continuous density between the C(4A) and C(4B) positions with only  $1.1$  Å between them.

The five-membered ring has a C(10) *endo*-envelope conformation, with C(10)  $0.569(5)$  Å from the plane through C(1), C(8), C(9), C(11). The four-membered ring C(1), C(2), C(7), C(8) is puckered, with deviations of  $\pm 0.064(5)$  Å from the ring plane; this corresponds to a  $13.2(4)^\circ$  fold about the C(1)···C(7) line. The methoxycarbonyl group at C(2) is oriented so that the atoms C(7), C(2), C(12), O(1), C(13) form an almost planar zig-zag fragment [torsion angles C(7)—C(2)—C(12)—O(1)  $172.9(4)$ , C(2)—C(12)—O(1)—C(13)  $-179.6(4)^\circ$ ]. This orientation places the carboxyl oxygen O(2)  $2.44$  Å from the H at C(7). Such an orientational preference is well known for  $\text{CH}_3\text{CO}_2$ -ester groups, which commonly orient themselves so as to have short intramolecular H···O=C contacts (Mathieson, 1965; Ferguson, Parvez, Cheung & Watson, 1983).

With the exception of those involving the disordered C(4) atom, the dimensions of the molecule are in accord with accepted values, with mean lengths  $C_{sp^3}-C_{sp^3}$   $1.539(5)$ ,  $C_{sp^3}-C_{sp^2}$   $1.499(5)$ , and  $C_{sp^2}=\text{O}$   $1.199(5)$  Å. There are no unusual intermolecular contacts and the molecules are separated by normal van der Waals distances.

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## References

- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- FERGUSON, G., PARVEZ, M., CHEUNG, A. T. C. & WATSON, T. R. (1983). *J. Chem. Res.* (S), 278–279; (M), 2539–2580.
- GABE, E. J., LARSON, A. C., WANG, Y. & LEE, F. L. (1981). *The NRC Crystal Structure Package*. National Research Council Laboratories, Ottawa, Canada.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- LANGE, G. L. (1983). In preparation.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- MATHIESON, A. M. (1965). *Tetrahedron Lett.* **46**, 4137–4140.
- ROBERTS, P. J. & SHELDRIK, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.