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Functionalized Hydrocarbons with Condensed Ring Skeletons: Methyl 1,10-*cis*-1,2-*transoid*-2,7-*cis*-8,14-Dioxotricyclo[8.4.0.$0^{2,7}$]tetradecane-1-carboxylate

By André G. Michel* and Nadine Michel-Dewez

Laboratoire de chimie structurale, Université de Sherbrooke, Sherbrooke (Québec), Canada J1K 2R1

and Réjean Ruel

Laboratoire de chimie organique, Université de Sherbrooke, Sherbrooke (Québec), Canada J1K 2R1

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Abstract. $C_{16}H_{22}O_4$, $M_r = 278{\cdot}35$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}2077\,(20)$, $b = 13{\cdot}6714\,(6)$, $c = 20{\cdot}5221\,(10)$ Å, $V = 2863{\cdot}93$ Å^3, $Z = 8$, two molecules in the asymmetric unit, $D_x = 1{\cdot}291$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54056$ Å, $\mu = 0{\cdot}71$ mm^{-1}, $F(000) = 1200$, room temperature, final $R = 0{\cdot}038$, $wR = 0{\cdot}026$, $S = 2{\cdot}70$ for 2857 significant reflections. The tricyclic compound bears a methoxycarbonyl group at position 1 [atom C(10)]. The relative stereochemistry is *cis* for the *AB* ring junction, *anti* between MeO_2C—C(10) and H—C(9) and *cis* for the *BC* ring junction; all-chair conformation is adopted.

Introduction. In the course of a general study on the conformational properties of tricyclic molecules having the tridecane skeleton, compound (1) (Fig. 1)† was synthesized using anionic cycloaddition (Ruel & Deslongchamps, 1989). The two C(8) epimers (1) and (2) were formed in equimolar quantities after treatment of enones (3) and (4) in a Cs_2CO_3 medium, followed by selective acid catalyzed decarboxylation. On the other hand, the treatment of a pure epimer (1) or (2) in acidic (PTSA,‡ benzene, reflux) or basic (*t*-butyl OK, *t*-butyl OH) conditions, leads to the formation of a (1:1) mixture of both epimers upon reaching equilibrium. Flash-chromatography allows the separation of (1) and (2) epimers [R_f: 0·41 and 0·37, respectively, in (1:1) ethyl acetate–hexanes]. In order to ascertain the structures of (1) and (2), the present crystallographic analysis was undertaken on compound (1) and further conformational energy calculations allowed us to deduce the molecular structure of compound (2).

Experimental. Crystal 0·30 × 0·20 × 0·20 mm; Enraf–Nonius CAD-4 diffractometer; graphite monochromator, Cu $K\alpha$ radiation; cell parameters were obtained by least-squares procedure on 30 reflections with 2θ angle in the range 60·0–120·0°. The $\omega/2\theta$ scan mode was used for data collection at a constant speed of 4° min^{-1}. A total of 3567 reflections was collected (3177 independent) up to $2\theta_{\max} = 143{\cdot}4°$, corresponding to $12 \geq h \geq 0$, $16 \geq k \geq 0$, $25 \geq l \geq 0$; 2857 reflections satisfying $I \geq 2{\cdot}5\sigma(I)$ were considered as observed. No correction was made for absorption, 80 standard reflections, 1% intensity variation. The *NRCVAX* system (Gabe, Lee & LePage, 1985) was used for all calculations. The structure was solved by the application of direct methods and refined by full-matrix least squares on *F*. Anisotropic thermal parameters were refined for non-H atoms. Function minimized: $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$. The H atoms were located from a difference map, their positions and isotropic temperature factors were refined. Weights based on counting statistics were used. The maximum Δ/σ ratio was 0·929 for the *z* coordinate of H(16*B*). In the last ΔF Fourier map, the deepest hole was $-0{\cdot}140$ e Å^{-3} and the highest peak $0{\cdot}190$ e Å^{-3}. Atomic scattering factors as stored in the *NRCVAX* program were those of Cromer & Waber (1974).

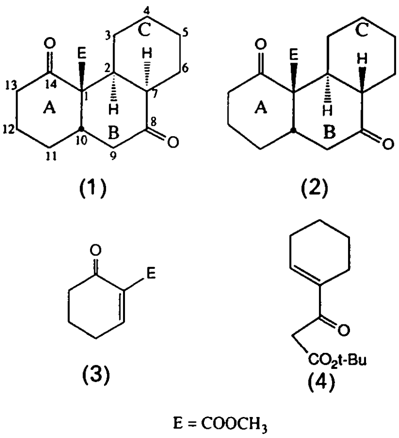

Fig. 1. Molecular formulae and atom numbering.

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* To whom correspondence should be addressed.

† Atomic numbering used in Fig. 1 does not correspond to that used for the crystallographic study.

‡ PTSA: *p*-toluenesulfonic acid.

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Table 1. *Final coordinates and equivalent B values, with e.s.d.'s in parentheses*

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}(Å^2)
Molecule 1				
O(1)	0·01921 (22)	0·03293 (14)	0·02616 (10)	4·06 (10)
O(2)	−0·3616 (3)	0·08473 (16)	0·18216 (9)	5·23 (13)
O(3)	−0·33975 (24)	−0·08745 (17)	−0·07606 (9)	4·46 (11)
O(4)	−0·16799 (23)	0·00566 (16)	−0·10283 (9)	4·11 (10)
C(1)	−0·0585 (3)	−0·03234 (21)	0·01475 (14)	2·92 (12)
C(2)	−0·0152 (4)	−0·1366 (3)	0·00719 (22)	4·40 (18)
C(3)	−0·0876 (5)	−0·2034 (3)	0·05528 (23)	4·88 (22)
C(4)	−0·2360 (4)	−0·18980 (24)	0·04987 (18)	3·98 (17)
C(5)	−0·2782 (3)	−0·08350 (22)	0·05699 (14)	2·86 (13)
C(6)	−0·2621 (4)	−0·04911 (24)	0·12833 (15)	3·44 (15)
C(7)	−0·2901 (3)	0·05691 (22)	0·13853 (13)	3·44 (14)
C(8)	−0·2197 (3)	0·12562 (22)	0·09334 (14)	2·88 (13)
C(9)	−0·2400 (3)	0·09561 (21)	0·02122 (13)	2·65 (12)
C(10)	−0·2070 (3)	−0·01357 (19)	0·00954 (12)	2·42 (11)
C(11)	−0·3780 (4)	0·12381 (23)	−0·00096 (16)	3·29 (14)
C(12)	−0·4050 (5)	0·2316 (3)	0·00974 (19)	4·52 (20)
C(13)	−0·3893 (5)	0·2606 (3)	0·08098 (19)	4·63 (18)
C(14)	−0·2521 (4)	0·23374 (24)	0·10434 (17)	3·88 (16)
C(15)	−0·2476 (3)	−0·03854 (20)	−0·06064 (13)	3·00 (13)
C(16)	−0·1992 (6)	−0·0087 (4)	−0·17245 (16)	5·51 (24)
Molecule 2				
O('1)	0·98366 (22)	0·99151 (17)	0·22696 (10)	4·35 (11)
O('2)	1·3728 (3)	0·98142 (18)	0·07031 (9)	5·73 (13)
O('3)	1·3267 (3)	1·11087 (18)	0·33923 (10)	5·57 (13)
O('4)	1·16171 (23)	1·00574 (16)	0·35602 (9)	4·17 (11)
C('1)	1·0553 (3)	1·05861 (24)	0·24193 (15)	3·35 (14)
C('2)	1·0039 (5)	1·1599 (3)	0·2543 (3)	5·31 (20)
C('3)	1·0718 (5)	1·2360 (3)	0·2129 (3)	6·0 (3)
C('4)	1·2219 (5)	1·2284 (3)	0·21978 (24)	5·12 (21)
C('5)	1·2728 (4)	1·12578 (25)	0·20552 (16)	3·55 (14)
C('6)	1·2628 (4)	1·1022 (3)	0·13194 (18)	4·22 (17)
C('7)	1·2967 (3)	0·9998 (3)	0·11482 (13)	3·75 (15)
C('8)	1·2303 (4)	0·9212 (3)	0·15380 (14)	3·26 (14)
C('9)	1·2471 (3)	0·94094 (21)	0·22771 (13)	2·75 (12)
C('10)	1·2052 (3)	1·04578 (21)	0·24655 (13)	2·72 (12)
C('11)	1·3877 (4)	0·91672 (24)	0·24801 (15)	3·40 (14)
C('12)	1·4250 (5)	0·8118 (3)	0·23030 (18)	4·37 (17)
C('13)	1·4088 (4)	0·7930 (3)	0·15739 (19)	4·55 (18)
C('14)	1·2713 (4)	0·8175 (3)	0·13597 (19)	4·36 (18)
C('15)	1·2406 (3)	1·05997 (22)	0·31909 (14)	3·36 (14)
C('16)	1·1829 (5)	1·0101 (4)	0·42693 (16)	5·02 (22)

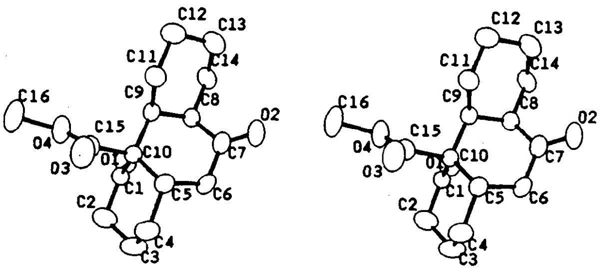

Fig. 2. *ORTEP* stereoscopic view (Johnson, 1976) of the crystal structure (1).

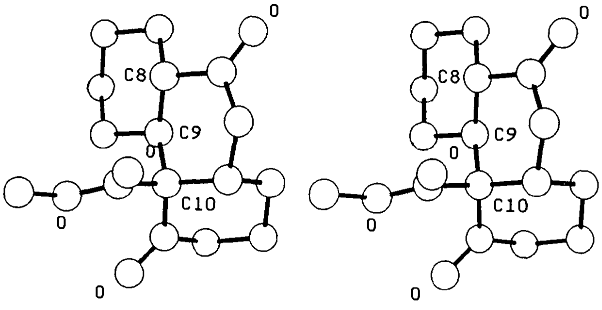

Fig. 3. Stereoview of the computer-generated structure of the CCC-8*S* epimer (2).

Table 2. *Molecular geometry*

(*a*) Intramolecular bond lengths (Å) with e.s.d.'s in parentheses

	Molecule 1	Molecule 2
O(1)—C(1)	1·217 (4)	1·212 (4)
O(2)—C(7)	1·216 (4)	1·225 (4)
O(3)—C(15)	1·196 (4)	1·195 (4)
O(4)—C(15)	1·333 (4)	1·332 (4)
O(4)—C(16)	1·477 (4)	1·472 (4)
C(1)—C(2)	1·501 (5)	1·502 (5)
C(1)—C(10)	1·541 (4)	1·544 (5)
C(2)—C(3)	1·534 (6)	1·513 (7)
C(3)—C(4)	1·530 (6)	1·542 (7)
C(4)—C(5)	1·523 (5)	1·524 (5)
C(5)—C(6)	1·546 (4)	1·547 (5)
C(5)—C(10)	1·546 (4)	1·543 (4)
C(6)—C(7)	1·492 (5)	1·485 (5)
C(7)—C(8)	1·503 (4)	1·501 (5)
C(8)—C(9)	1·550 (4)	1·550 (4)
C(8)—C(14)	1·531 (5)	1·523 (5)
C(9)—C(10)	1·549 (4)	1·545 (4)
C(9)—C(11)	1·530 (5)	1·530 (5)
C(10)—C(15)	1·537 (4)	1·544 (4)
C(11)—C(12)	1·515 (5)	1·529 (5)
C(12)—C(13)	1·523 (6)	1·527 (5)
C(13)—C(14)	1·525 (6)	1·508 (6)

(*b*) Valence angles (°) with e.s.d.'s in parentheses

	Molecule 1	Molecule 2
C(15)—O(4)—C(16)	115·9 (3)	116·8 (3)
O(1)—C(1)—C(2)	121·6 (3)	122·0 (3)
O(1)—C(1)—C(10)	122·2 (3)	121·8 (3)
C(2)—C(1)—C(10)	116·2 (3)	116·1 (3)
C(1)—C(2)—C(3)	110·9 (3)	112·3 (4)
C(2)—C(3)—C(4)	110·9 (3)	110·9 (4)
C(3)—C(4)—C(5)	112·9 (3)	112·6 (3)
C(4)—C(5)—C(6)	110·5 (3)	110·9 (3)
C(4)—C(5)—C(10)	113·4 (3)	113·3 (3)
C(6)—C(5)—C(10)	110·99 (25)	110·8 (3)
C(5)—C(6)—C(7)	114·07 (25)	114·3 (3)
O(2)—C(7)—C(6)	121·5 (3)	121·2 (3)
O(2)—C(7)—C(8)	123·1 (3)	122·5 (3)
C(6)—C(7)—C(8)	115·4 (3)	116·3 (3)
C(7)—C(8)—C(9)	111·10 (24)	110·3 (3)
C(7)—C(8)—C(14)	114·2 (3)	114·4 (3)
C(9)—C(8)—C(14)	111·6 (3)	111·5 (3)
C(8)—C(9)—C(10)	111·95 (23)	112·07 (24)
C(8)—C(9)—C(11)	109·9 (3)	109·4 (3)
C(10)—C(9)—C(11)	113·41 (25)	113·09 (25)
C(1)—C(10)—C(5)	108·41 (24)	109·2 (3)
C(1)—C(10)—C(9)	111·34 (24)	111·39 (25)
C(1)—C(10)—C(15)	107·07 (23)	106·09 (24)
C(5)—C(10)—C(9)	113·32 (24)	113·42 (25)
C(5)—C(10)—C(15)	109·01 (23)	109·41 (25)
C(9)—C(10)—C(15)	107·48 (22)	107·03 (23)
C(9)—C(11)—C(12)	111·7 (3)	111·8 (3)
C(11)—C(12)—C(13)	111·9 (3)	111·3 (3)
C(12)—C(13)—C(14)	109·6 (3)	110·4 (3)
C(8)—C(14)—C(13)	112·6 (3)	113·1 (3)
O(3)—C(15)—O(4)	124·1 (3)	124·9 (3)
O(3)—C(15)—C(10)	125·7 (3)	125·4 (3)
O(4)—C(15)—C(10)	110·08 (25)	109·7 (3)

Discussion. Table 1 gives the final atomic parameters for the two independent molecules of the asymmetric unit with their B_{eq} values.* Fig. 1 gives the molecular formulae and atom numbering. Fig. 2 shows a stereoscopic view of molecule 1. Bond lengths and angles are given in Table 2. Very small differences can be observed between the two molecules. The crystal structure shows that rings *A*, *B* and *C* have chair conformations. The methoxycarbonyl group at

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and all torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52285 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C(10) and the alkyl chain at C(8) are equatorial in ring *B* while the chain at C(9) is axial. Presumably, such a conformation avoids strong 1,3-diaxial interactions between the methoxycarbonyl group and the C(8)—C(9) region of ring *B*. This conformation corresponds to one epimer in the (1:1) mixture after equilibration and this molecular structure was used to determine the second epimeric structure. Total conformational energies of possible structures for C(8) epimers have been calculated using the *MAXIMIN* program of the *SYBYL* molecular modeling system (Tripos Associates, 1988). The structure CCC-8*R** observed for the crystal structure corresponds to the global minimum for this structure ($-26{\cdot}4$ kJ mol^{-1}). Another possible isomer was CBC-8*S* obtained by modification of the conformation of ring *B* (chair→boat) and inversion of carbon C(8). The corresponding energy was much higher ($-2{\cdot}9$ kJ mol^{-1}) due to torsional contributions at the C(10)—C(9) bond. The CCC-8*S* epimer (2) structure was obtained by inversion of the C(8) center, reorganization of the rings and energy minimization. The inversion at C(8) induces extensive reorganization involving rings *A* and *B* in order to reach an all-chair conformation with conformational energy of $-23{\cdot}9$ kJ mol^{-1}. Similar values of conformational energies obtained for the crystalline structure of (1) (Fig. 2) and the computer-generated structure of (2) (Fig.3) account for the 1:1 equilibration.

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* CCC-8*R* is the abbreviation of chair (ring *A*), chair (ring *B*), chair (ring *C*) with the C(8) in the *R* configuration. The meaning of further similar abbreviations can be easily deduced.

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Structure of Butyldodecyldimethylammonium Bromide Monohydrate

By Tooru Taga, Yoshihisa Miwa and Katsunosuke Machida

Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606, *Japan*

and Noriyuki Kimura, Soichiro Hayashi, Junzo Umemura and Tohru Takenaka

Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, *Japan*

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Abstract. $C_{18}H_{40}N^+.Br^-.H_2O$, $M_r = 368{\cdot}4$, triclinic, $P\bar{1}$, $a = 8{\cdot}164\,(1)$, $b = 8{\cdot}486\,(2)$, $c = 17{\cdot}531\,(1)$ Å, $\alpha = 74{\cdot}72\,(1)$, $\beta = 86{\cdot}28\,(1)$, $\gamma = 71{\cdot}57\,(1)°$, $V = 1111{\cdot}3\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}10$ Mg m^{-3}, λ(Cu $K\alpha$) $= 1{\cdot}54178$ Å, $\mu = 2{\cdot}5$ mm^{-1}, $F(000) = 400$, $T = 295$ K, $R = 0{\cdot}061$ for 2695 reflections. The molecules are packed in bilayers parallel to the (001) plane. The Br ions and water molecules form an anionic group. The Br···O hydrogen-bond distances are 3·410 (1) and 3·414 (1) Å.

Introduction. The structure of the title crystal was determined as part of our continuing studies on the crystal properties and molecular packing of alkylammonium halides with various alkyl chain lengths. The molecule has a butyl group as the secondary long hydrocarbon chain which is different from that of the dodecyldimethylpropylammonium bromides studied so far (Taga, Machida, Kimura, Hayashi, Umemura & Takenaka, 1986, 1987). Thus the crystal structure allows a comparison of the effects of the different chain lengths on the molecular packing in these crystal structures.

Experimental. Crystals grown from ethyl acetate solution; colorless prism; 0·2 × 0·2 × 0·15 mm; Rigaku AFC-5RU diffractometer with graphite-monochromated Cu $K\alpha$ radiation; lattice parameters from 22 reflections with $18{\cdot}8 < \theta < 27{\cdot}2°$; 3677 reflections measured within $2\theta < 120°$; $-9 \le h \le 0$,

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