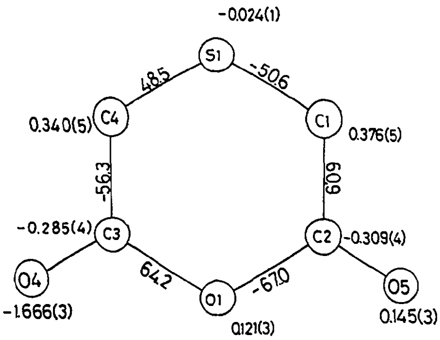

Fig. 2. Endocyclic torsional angles (°) and distances (Å) of the atoms from the mean plane through the ring.

values (Barnes, Paton & McKissock, 1983). The exocyclic mean C_{methyl}—O, C_{ring}—O and S—O bond lengths of 1·431 (7), 1·389 (6) and 1·435 (4) Å agree with the values given for these bond distances (*International Tables for X-ray Crystallography*, 1962, Vol. III). The O—S—O, C—S—O and C—S—C angles are in the range 100·5 (2)–117·8 (2)°, consistent with the expected tetrahedral geometry. The oxathiane ring is in a chair conformation as can be seen from the endocyclic torsional angles given in Fig. 2. However, the C—S—C part is more flattened than the C—O—C part. The mean absolute value of S(1)—C(1)—C(2)—O(1) and S(1)—C(4)—C(3)—O(1) is 58·6°, the mean of C(4)—C(3)—O(1)—C(2) and C(1)—C(2)—O(1)—C(3) is 65·6°, whereas for C(3)—C(4)—S(1)—C(1) and C(2)—C(1)—S(1)—C(4) it is 49·6°. Other numerical values given in Fig. 2 are the distances of the atoms from the mean planes through the ring. Hence we conclude that the O(4) atom is in an axial position and O(5) in an equatorial position, and that the title compound crystallizes in the *trans* configuration. The torsion angles C(5)—O(4)—C(3)—C(4) and C(6)—O(5)—C(2)—C(1) are 163·7 (4) and 170·9 (4)°, respectively.

The crystal packing is determined by van der Waals contacts.

We thank Professor A. Conde for useful discussions, and the Junta de Andalucía and DGICYT, PB89-0540, for financial support.

References

Barnes, J. C., Paton, J. D. & McKissock, A. (1983). *Acta Cryst.* C39, 547–550.
Campos, A. L. (1989). PhD Thesis, Univ. of Seville, Spain.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
Nardelli, M. (1983). *Acta Cryst.* C39, 1141–1142.
Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). The *XRAY76* system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

Acta Cryst. (1991). C47, 1032–1036

Functionalized Hydrocarbons with Condensed Ring Skeletons. VI. A Tricyclo[8.4.0.0^{3,8}]tetradec-1-ene and its Parent Fourteen-Membered Dimethyl Macrocycle

By André G. Michel,* Marc Drouin and Nadine Michel-Dewez

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

and Andrew Roughton and Pierre Deslongchamps

Laboratoire de synthèse organique, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

(*Received* 19 *April* 1990; *accepted* 5 *September* 1990)

Abstract. $C_{24}H_{34}O_8$, $M_r = 450{\cdot}52$, $\lambda(\mathrm{Cu}\ K\bar{\alpha}) = 1{\cdot}54056$ Å, room temperature. (I) Tetramethyl (3*Z*,5*E*,11*E*)-3,11-dimethylcyclotetradeca-3,5,11-triene-1,1,8,8-tetracarboxylate, monoclinic, $P2_1/a$, $a = 13{\cdot}5494$ (8), $b = 14{\cdot}739$ (3), $c = 13{\cdot}6734$ (10) Å, $\beta = 117{\cdot}340$ (5)°, $V = 2425{\cdot}6$ (5) Å^3, $Z = 4$, $D_x = 1{\cdot}234$ Mg m^{-3}, $\mu = 0{\cdot}72$ mm^{-1}, $F(000) = 967{\cdot}90$, final $R = 0{\cdot}045$ for 3780 observed reflections. (II) Tetramethyl 3,8-*cis*-8,9-*transoid*-9,14-*cis*-1,7-di-methyltricyclo[8.4.0.0^{3,8}]tetradec-1-ene-5,5,12,12-tetracarboxylate (alternative name: tetramethyl 3,9-dimethyltricyclo[8.4.0.0^{2,7}]tetradec-8-ene-5,5,12,12-tetracarboxylate), monoclinic, $P2_1/c$, $a = 9{\cdot}287$ (1), $b = 18{\cdot}460$ (2), $c = 27{\cdot}7976$ (9) Å, $\beta = 98{\cdot}119$ (9)°, $V = 4717{\cdot}8$ (7) Å^3, $Z = 8$, $D_x = 1{\cdot}269$ Mg m^{-3}, $\mu = 0{\cdot}74$ mm^{-1}, $F(000) = 1935{\cdot}79$, final $R = 0{\cdot}087$ for

---

* To whom correspondence should be addressed.

0108-2701/91/051032-05$03.00

6051 observed reflections. Subjecting the fourteen-membered macrocycle (I) to conditions of the thermally induced Diels–Alder reaction afforded an unexpected tricyclic adduct (II). Both (I) and (II) contain two pairs of methyl esters at C(5) and C(12) in addition to methyl groups at C(1) and C(7). The diene segment of (I) is comprised of $\Delta^{9,10}$ *trans* and $\Delta^{7,8}$ *cis* double bonds as in previously reported similar compounds. The *trans* $\Delta^{1,2}$ double bond of the dienophile portion forces this moiety to adopt a synclinal form of butene. The steroid-like condensed ring skeleton of (II) includes chair conformations in rings *A* and *C* while ring *B* prefers a half-chair conformation from which the C(15) methyl group extends equatorially outwards. The C(7) methyl group sits axially on ring *C* despite the conformational mobility afforded by the *cis–anti–cis* relative stereochemistry. The crystallographic study herein provides the fundamental bases of a possible explanation linking macrocycle (I) with its unanticipated tricyclic adduct (II).

Introduction. Earlier papers in this series (Michel, Michel-Dewez, Roughton, Springer & Hoogsteen, 1989*a*,*b*; Michel, Michel-Dewez & Roughton, 1989; Michel, Boulay & Marinier, 1989; Michel, Proulx & Michel-Dewez, 1988) have dealt with macrocyclic and tricyclic structures derived from high yielding macrocyclizations through S_N2 displacement and [4+2] cycloaddition. A systematic study of substituted macrocycles has led to identification of those substitution patterns and macrocyclic triene geometries that show great potential for the construction of complex polycyclic molecules (Lamothe, Ndibwami & Deslongchamps, 1988*a*), including the recent development of indirect access to the *trans–anti–trans* tricycle stereochemistry so often seen in natural products (Marinier & Deslongchamps, 1988). Certain systems, however, have also proven to be problematic in that products of unknown structure have been produced at the expense of the desired and predicted adducts, isolated either in low yields or not at all. Macrocycle (I) was prepared from the appropriate allylic chloride triene (Roughton, 1988) and heated to 578 K for 2 h. Although a number of theoretical transition-state interactions were recognized as potentially disfavouring, a single racemic Diels–Alder diastereomer (III) (Fig. 1) was predicted. A crystalline product was obtained in 66% isolated (non-optimized) yield. Puzzling NMR data suggested, however, that the expected tricycle (III) had not been produced, whereupon the present crystallographic studies were undertaken in the hope of securing both the structures and conformations.

Experimental. Crystals 0·10 × 0·15 × 0·30 mm; Enraf–Nonius CAD-4 diffractometer; graphite monochromator; Cu $K\alpha$ radiation; cell parameters were obtained by least-squares procedures on 24 reflections with 2θ angle in the range 60·00–100·00°. One standard reflection monitored every 100 reflections without significant deviation. The $\omega/2\theta$ scan mode was used for data collection at a constant scan speed of 4° min^{-1}; $2\theta_{\max} = 143{\cdot}9°$.

(I) $-16 \le h \le 14$, $0 \le k \le 17$, $0 \le l \le 16$; 4752 unique measured reflections, 3780 observed with $I \ge 2{\cdot}5\sigma(I)$; $w = 1/\sigma^2(F)$, $R = 0{\cdot}045$, $wR = 0{\cdot}028$; max. $\Delta/\sigma = 0{\cdot}17$; max. and min. density peak = 0·27 and $-0{\cdot}24$ e Å^{-3}.

(II) $-10 \le h \le 10$, $0 \le k \le 22$, $0 \le l \le 34$; 10 312 unique measured reflections, 6051 observed with $I \ge 2{\cdot}5\sigma(I)$; $w = 1/\sigma^2(F)$, $R = 0{\cdot}087$, $wR = 0{\cdot}059$, max. $\Delta/\sigma = 0{\cdot}37$; max. and min. density peak = 0·47 and $-0{\cdot}41$ e Å^{-3}. The relatively high rotational mobilities of methyl esters prevent a better refinement.

The *NRCVAX* system was used for all calculations (Gabe, Lee & LePage, 1985). 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. The H atoms were located from a difference map and refined with isotropic thermal factors for (I), but not refined for (II).

Discussion. Final atomic parameters are given in Table 1.* Bond lengths and valence angles are given in Table 2. Fig. 1 shows the molecular schemes. Perspective views of both title compounds are depicted in Fig. 2. The structure determination of (I) indicates that the double bonds $\Delta^{9,10}$, $\Delta^{7,8}$ and $\Delta^{1,2}$ are indeed *trans*, *cis* and *trans* respectively (Fig. 2), confirming that tricycle (II) originates from this macrocyclic triene configuration. While the planar *trans–cis* diene portion of this macrocycle appears entirely analogous to those reported earlier (Michel, Michel-Dewez, Roughton, Springer & Hoogsteen, 1989*a*), the *trans* dienophile portion takes a considerably different conformation here as compared to that of the *cis* analogue. The C(15) methyl group appears to protrude outside the ring in a direction roughly opposite to that of the C(16) methyl. The torsion angle C(2)—C(3)—C(4)—C(5) is 154·1 (2)°, indicating a considerable break from planarity for this portion of the molecule; the same series in *cis* dienophiles is relatively planar (torsion angle approx. 170–177°). Similarly, the C(1)—C(14)—C(13)—C(12) series of (I) has a torsion angle of −73·8 (1)°. Particularly noteworthy is the series C(2)—C(1)—C(14)—

---

* Lists of structure factors, anisotropic thermal parameters, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53553 (78 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final coordinates and* B_{eq} *values for non*-H *atoms with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq}(Å^2)
(I)				
O(1)	0·3701 (1)	0·2697 (1)	0·1320 (1)	5·63 (9)
O(2)	0·3119 (1)	0·2881 (1)	0·2589 (1)	5·49 (9)
O(3)	0·1614 (1)	0·0895 (1)	0·2349 (1)	5·02 (9)
O(4)	0·3325 (1)	0·0778	0·2486 (1)	4·24 (8)
O(5)	−0·1849 (1)	0·4424	−0·4487 (1)	4·98 (8)
O(6)	−0·3620 (1)	0·4294	−0·4826 (1)	4·29 (7)
O(7)	−0·3864 (1)	0·2069 (1)	−0·4161 (1)	7·5 (1)
O(8)	−0·3206 (1)	0·2338 (1)	−0·5360 (1)	6·4 (1)
C(1)	−0·0684 (2)	0·4081 (1)	−0·1282 (2)	3·3 (1)
C(2)	−0·0307 (2)	0·3466 (1)	−0·0490 (2)	3· (1)
C(3)	0·0891 (2)	0·3228 (1)	0·0247 (2)	3·7 (1)
C(4)	0·1009 (2)	0·2328 (2)	0·0849 (2)	3·4 (1)
C(5)	0·2122 (1)	0·1831 (1)	0·1187 (1)	2·9 (9)
C(6)	0·2177 (2)	0·1370 (1)	0·0185 (2)	2·0 (1)
C(7)	0·1281 (2)	0·0684 (1)	−0·0439 (1)	3·05 (9)
C(8)	0·0365 (2)	0·0872 (1)	−0·1367 (2)	3·4 (1)
C(9)	0·0044 (2)	0·1727 (1)	−0·1951 (2)	3·4 (1)
C(10)	−0·0931 (2)	0·1905 (1)	−0·2795 (2)	3·7 (1)
C(11)	−0·1222 (2)	0·2779 (2)	−0·3418 (2)	3·7 (1)
C(12)	−0·2381 (2)	0·3163 (1)	−0·3701 (2)	3·37 (9)
C(13)	−0·2553 (2)	0·3390 (2)	−0·2689 (2)	3·8 (1)
C(14)	−0·1914 (2)	0·4208 (2)	−0·1998 (2)	3·8 (1)
C(15)	0·0079 (3)	0·4687 (2)	−0·1504 (3)	5·3 (2)
C(16)	0·1481 (2)	−0·0266 (2)	0·0025 (2)	4·5 (1)
C(17)	0·3079 (2)	0·2508 (1)	0·1680 (2)	3·7 (1)
C(18)	0·3966 (3)	0·3583 (3)	0·3102 (4)	8·2 (2)
C(19)	0·2297 (2)	0·1122 (1)	0·2072 (2)	3·5 (1)
C(20)	0·3583 (3)	0·0067 (3)	0·3311 (3)	6·3 (2)
C(21)	−0·2559 (2)	0·4022 (1)	−0·4384 (1)	3·5 (1)
C(22)	−0·3887 (3)	0·5085 (2)	−0·5546 (2)	4·9 (2)
C(23)	−0·3254 (2)	0·2464 (2)	−0·4412 (2)	4·6 (1)
C(24)	−0·3953 (4)	0·1670 (2)	−0·6137 (4)	9·2 (2)
(II) Molecule 1				
C(1)	0·4471 (5)	0·3148 (2)	0·2343 (2)	3·3 (2)
C(2)	0·5174 (5)	0·3083 (2)	0·2787 (2)	3·5 (2)
C(3)	0·5431 (5)	0·2382 (2)	0·3058 (2)	3·29 (2)
C(4)	0·4467 (5)	0·2352 (2)	0·3468 (2)	3·58 (2)
C(5)	0·4534 (5)	0·1635 (2)	0·3750 (2)	3·6 (2)
C(6)	0·4328 (5)	0·0991 (2)	0·3392 (2)	4·0 (3)
C(7)	0·5339 (6)	0·1019 (2)	0·2995 (2)	4·0 (3)
C(8)	0·5170 (5)	0·1733 (2)	0·2712 (2)	3·2 (2)
C(9)	0·3693 (5)	0·1847 (2)	0·2386 (1)	2·9 (2)
C(10)	0·3124 (5)	0·1192 (2)	0·2074 (2)	3·8 (2)
C(11)	0·4053 (5)	0·1013 (2)	0·1673 (2)	3·9 (2)
C(12)	0·4061 (5)	0·1666 (3)	0·1332 (2)	3·5 (2)
C(13)	0·4612 (5)	0·2350 (2)	0·1615 (1)	3·4 (2)
C(14)	0·3790 (5)	0·2506 (2)	0·2056 (2)	3·2 (2)
C(15)	0·4295 (5)	0·3879 (2)	0·2092 (2)	4·7 (3)
C(16)	0·6933 (6)	0·0850 (3)	0·3183 (2)	5·4 (3)
C(17)	0·5918 (7)	0·1512 (3)	0·4109 (2)	4·8 (3)
C(18)	0·8130 (6)	0·1981 (3)	0·4502 (2)	7·8 (4)
C(19)	0·3230 (7)	0·1634 (3)	0·4034 (2)	5·0 (3)
C(20)	0·2444 (7)	0·2007 (3)	0·4766 (2)	9·0 (4)
C(21)	0·5112 (6)	0·1512 (3)	0·0963 (2)	4·7 (3)
C(22)	0·5920 (7)	0·1912 (3)	0·0236 (2)	7·6 (4)
C(23)	0·2551 (7)	0·1807 (3)	0·1041 (2)	5·1 (3)
C(24)	0·0503 (7)	0·1354 (4)	0·0553 (2)	10·6 (5)
O(1)	0·6764 (4)	0·2101 (2)	0·4171 (1)	5·2 (2)
O(2)	0·6222 (5)	0·0951 (2)	0·4314 (1)	6·7 (2)
O(3)	0·3641 (4)	0·1901 (2)	0·4476 (1)	6·7 (2)
O(4)	0·2021 (4)	0·1475 (2)	0·3882 (2)	8·2 (3)
O(5)	0·4890 (4)	0·1956 (2)	0·0590 (1)	6·5 (2)
O(6)	0·6060 (5)	0·1079 (2)	0·1015 (1)	9·7 (3)
O(7)	0·1988 (4)	0·1210 (2)	0·0840 (1)	7·2 (2)
O(8)	0·1970 (5)	0·2389 (2)	0·0999 (1)	7·7 (2)
(II) Molecule 2				
C′(1)	0·9341 (5)	0·2515 (2)	0·2311 (2)	3·6 (2)
C′(2)	1·0049 (5)	0·2553 (2)	0·2754 (2)	3·6 (2)
C′(3)	1·0401 (5)	0·3255 (2)	0·3027 (2)	3·4 (2)
C′(4)	0·9442 (5)	0·3316 (2)	0·3436 (2)	3·5 (2)
C′(5)	0·9621 (5)	0·4036 (2)	0·3720 (2)	3·4 (2)
C′(6)	0·9503 (5)	0·4684 (2)	0·3364 (1)	3·3 (2)
C′(7)	1·0508 (5)	0·4628 (2)	0·2967 (2)	3·3 (2)
C′(8)	1·0246 (5)	0·3911 (2)	0·2680 (1)	3·0 (2)
C′(9)	0·8764 (5)	0·3852 (2)	0·2347 (1)	3·0 (2)
C′(10)	0·8302 (5)	0·4516 (2)	0·2030 (2)	3·6 (2)
C′(11)	0·9263 (5)	0·4646 (2)	0·1634 (2)	4·0 (3)
C′(12)	0·9223 (6)	0·3983 (3)	0·1300 (2)	4·2 (3)
C′(13)	0·9677 (5)	0·3299 (3)	0·1599 (2)	4·0 (2)
C′(14)	0·8775 (5)	0·3177 (2)	0·2021 (2)	3·37 (2)
C′(15)	0·9039 (5)	0·1798 (2)	0·2057 (2)	4·8 (3)
C′(16)	1·2121 (5)	0·4740 (3)	0·3156 (2)	4·7 (3)
C′(17)	1·1047 (6)	0·4045 (3)	0·4079 (2)	4·1 (3)
C′(18)	1·2525 (6)	0·4768 (3)	0·4655 (2)	6·1 (3)
C′(19)	0·8426 (6)	0·4057 (3)	0·4043 (2)	3·9 (3)
C′(20)	0·5924 (5)	0·4247 (3)	0·4064 (2)	5·1 (3)
C′(21)	1·0290 (6)	0·4076 (3)	0·0931 (2)	7·3 (4)
C′(22)	1·2 (1)	0·4257 (6)	0·0785 (3)	7·2 (7)
C′(23)	0·7724 (7)	0·3867 (3)	0·1000 (2)	5·8 (3)
C′(24)	0·5807 (8)	0·4404 (4)	0·0521 (2)	14·7 (5)
O′(1)	1·1241 (4)	0·4687 (2)	0·4295 (1)	4·9 (2)
O′(2)	1·1862 (4)	0·3550 (2)	0·4153 (1)	6·7 (2)
O′(3)	0·7137 (4)	0·4232 (2)	0·3794 (1)	4·6 (2)
O′(4)	0·8581 (4)	0·3908 (2)	0·4465 (1)	6·7 (2)
O′(5)	1·1584 (4)	0·4227 (2)	0·1091 (1)	8·6 (3)
O′(6)	0·9904 (9)	0·4496 (4)	0·0556 (3)	10·5 (6)
O′(7)	0·7131 (5)	0·4462 (2)	0·0853 (2)	9·6 (3)
O′(8)	0·7234 (6)	0·3303 (3)	0·0886 (2)	13·9 (4)

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

(I)

O(1)—C(17)	1·188 (3)	C(3)—C(4)	1·531 (3)
O(2)—C(17)	1·337 (3)	C(4)—C(5)	1·545 (3)
O(2)—C(18)	1·463 (3)	C(5)—C(6)	1·560 (3)
O(3)—C(19)	1·198 (3)	C(5)—C(17)	1·526 (3)
O(4)—C(19)	1·338 (2)	C(5)—C(19)	1·533 (3)
O(4)—C(20)	1·460 (3)	C(6)—C(7)	1·509 (3)
O(5)—C(21)	1·192 (3)	C(7)—C(8)	1·334 (3)
O(6)—C(21)	1·339 (2)	C(7)—C(16)	1·509 (3)
O(6)—C(22)	1·460 (3)	C(8)—C(9)	1·447 (3)
O(7)—C(23)	1·184 (3)	C(9)—C(10)	1·321 (3)
O(8)—C(23)	1·341 (3)	C(10)—C(11)	1·494 (3)
O(8)—C(24)	1·461 (3)	C(11)—C(12)	1·543 (3)
C(1)—C(2)	1·323 (3)	C(12)—C(13)	1·541 (3)
C(1)—C(14)	1·507 (3)	C(12)—C(21)	1·526 (3)
C(1)—C(15)	1·499 (3)	C(12)—C(23)	1·533 (3)
C(2)—C(3)	1·507 (3)	C(13)—C(14)	1·531 (3)

C(17)—O(2)—C(18)	115·1 (3)	C(9)—C(10)—C(11)	124·4 (2)
C(19)—O(4)—C(20)	115·6 (2)	C(10)—C(11)—C(12)	115·5 (2)
C(21)—O(6)—C(22)	115·2 (2)	C(11)—C(12)—C(13)	114·3 (2)
C(23)—O(8)—C(24)	118·1 (3)	C(11)—C(12)—C(21)	108·3 (2)
C(2)—C(1)—C(14)	120·8 (2)	C(11)—C(12)—C(23)	108·2 (2)
C(2)—C(1)—C(15)	122·1 (2)	C(13)—C(12)—C(21)	108·9 (2)
C(14)—C(1)—C(15)	117·1 (2)	C(13)—C(12)—C(23)	108·9 (2)
C(1)—C(2)—C(3)	126·8 (2)	C(21)—C(12)—C(23)	108·1 (2)
C(2)—C(3)—C(4)	112·1 (2)	C(12)—C(13)—C(14)	116·7 (2)
C(3)—C(4)—C(5)	114·7 (2)	C(1)—C(14)—C(13)	116·5 (2)
C(4)—C(5)—C(6)	112·2 (1)	O(1)—C(17)—O(2)	123·7 (2)
C(4)—C(5)—C(17)	109·7 (2)	O(1)—C(17)—C(5)	126·3 (2)
C(4)—C(5)—C(19)	109·6 (2)	O(2)—C(17)—C(5)	110·1 (2)
C(6)—C(5)—C(17)	107·4 (2)	O(3)—C(19)—O(4)	124·5 (2)
C(6)—C(5)—C(19)	110·1 (2)	O(3)—C(19)—C(5)	125·3 (2)
C(17)—C(5)—C(19)	107·8 (1)	O(4)—C(19)—C(5)	110·2 (2)
C(5)—C(6)—C(7)	116·0 (2)	O(5)—C(21)—O(6)	123·7 (2)
C(6)—C(7)—C(8)	123·6 (2)	O(5)—C(21)—C(12)	125·1 (2)
C(6)—C(7)—C(16)	116·2 (2)	O(6)—C(21)—C(12)	111·1 (2)
C(8)—C(7)—C(16)	120·1 (2)	O(7)—C(23)—O(8)	124·2 (2)
C(7)—C(8)—C(9)	128·2 (2)	O(7)—C(23)—C(12)	125·8 (2)
C(8)—C(9)—C(10)	125·6 (2)	O(8)—C(23)—C(12)	109·9 (2)

(II)

	Mol. 1	Mol. 2
C(1)—C(2)	1·320 (6)	1·314 (6)
C(1)—C(14)	1·516 (6)	1·515 (6)
C(1)—C(15)	1·515 (6)	1·507 (6)
C(2)—C(3)	1·498 (6)	1·513 (6)
C(3)—C(4)	1·548 (6)	1·544 (7)
C(3)—C(8)	1·534 (6)	1·542 (6)
C(4)—C(5)	1·533 (6)	1·542 (6)
C(5)—C(6)	1·546 (6)	1·546 (6)
C(5)—C(17)	1·529 (7)	1·543 (7)
C(5)—C(19)	1·537 (8)	1·524 (7)
C(6)—C(7)	1·546 (7)	1·547 (6)
C(7)—C(8)	1·532 (6)	1·547 (6)
C(7)—C(16)	1·530 (7)	1·530 (7)
C(8)—C(9)	1·548 (6)	1·549 (6)
C(9)—C(10)	1·538 (6)	1·535 (6)

Table 2 (*cont.*)

	Mol. 1	Mol. 2
C(9)—C(14)	1·533 (6)	1·542 (6)
C(10)—C(11)	1·540 (7)	1·531 (7)
C(11)—C(12)	1·533 (6)	1·533 (6)
C(12)—C(13)	1·536 (6)	1·536 (7)
C(12)—C(21)	1·539 (7)	1·533 (7)
C(12)—C(23)	1·538 (8)	1·533 (8)
C(13)—C(14)	1·559 (6)	1·551 (7)
C(17)—O(1)	1·339 (7)	1·330 (6)
C(17)—O(2)	1·196 (6)	1·185 (6)
C(18)—O(1)	1·475 (6)	1·452 (6)
C(19)—O(3)	1·330 (6)	1·334 (6)
C(19)—O(4)	1·180 (7)	1·193 (5)
C(20)—O(3)	1·475 (7)	1·439 (6)
C(21)—O(5)	1·316 (6)	1·252 (7)
C(21)—O(6)	1·183 (7)	1·309 (8)
C(22)—O(5)	1·467 (6)	1·367 (1)
C(23)—O(7)	1·312 (7)	1·269 (7)
C(23)—O(8)	1·200 (7)	1·164 (8)
C(24)—O(7)	1·517 (7)	1·433 (7)
C(2)—C(1)—C(14)	122·3 (4)	123·1 (4)
C(2)—C(1)—C(15)	121·3 (4)	121·4 (4)
C(14)—C(1)—C(15)	116·4 (4)	115·6 (4)
C(1)—C(2)—C(3)	124·9 (4)	124·0 (4)
C(2)—C(3)—C(4)	109·5 (4)	109·0 (4)
C(2)—C(3)—C(8)	111·1 (3)	111·4 (3)
C(4)—C(3)—C(8)	112·1 (4)	112·9 (3)
C(3)—C(4)—C(5)	114·9 (4)	114·1 (4)
C(4)—C(5)—C(6)	110·1 (3)	110·3 (3)
C(4)—C(5)—C(17)	115·6 (4)	111·2 (4)
C(4)—C(5)—C(19)	106·6 (4)	106·8 (4)
C(6)—C(5)—C(17)	108·8 (4)	112·5 (4)
C(6)—C(5)—C(19)	107·2 (4)	111·4 (4)
C(17)—C(5)—C(19)	108·3 (4)	104·4 (4)
C(5)—C(6)—C(7)	113·6 (4)	114·2 (3)
C(6)—C(7)—C(8)	111·5 (4)	110·9 (3)
C(6)—C(7)—C(16)	114·0 (4)	113·9 (3)
C(8)—C(7)—C(16)	112·0 (4)	111·6 (4)
C(3)—C(8)—C(7)	110·8 (3)	110·9 (3)
C(3)—C(8)—C(9)	108·0 (3)	108·4 (3)
C(7)—C(8)—C(9)	115·9 (4)	115·4 (3)
C(8)—C(9)—C(10)	115·4 (3)	116·1 (4)
C(8)—C(9)—C(14)	109·7 (3)	109·2 (3)
C(10)—C(9)—C(14)	109·3 (3)	109·4 (3)
C(9)—C(10)—C(11)	113·2 (4)	113·2 (4)
C(10)—C(11)—C(12)	109·3 (4)	110·1 (4)
C(11)—C(12)—C(13)	111·1 (3)	110·3 (3)
C(11)—C(12)—C(21)	108·9 (4)	110·6 (4)
C(11)—C(12)—C(23)	112·0 (4)	112·5 (4)
C(13)—C(12)—C(21)	107·2 (4)	107·5 (4)
C(13)—C(12)—C(23)	110·0 (4)	109·8 (4)
C(21)—C(12)—C(23)	107·3 (4)	105·9 (4)
C(12)—C(13)—C(14)	112·9 (4)	113·2 (4)
C(1)—C(14)—C(9)	111·2 (3)	111·7 (3)
C(1)—C(14)—C(13)	110·1 (4)	109·6 (4)
C(9)—C(14)—C(13)	113·6 (3)	112·1 (4)
C(5)—C(17)—O(1)	112·8 (4)	110·6 (4)
C(5)—C(17)—O(2)	124·1 (5)	124·9 (5)
O(1)—C(17)—O(2)	123·1 (5)	124·5 (5)
C(5)—C(19)—O(3)	109·3 (5)	112·0 (4)
C(5)—C(19)—O(4)	126·6 (5)	125·2 (5)
O(3)—C(19)—O(4)	123·8 (5)	122·7 (5)
C(12)—C(21)—O(5)	111·5 (4)	117·8 (4)
C(12)—C(21)—O(6)	125·2 (5)	118·0 (6)
O(5)—C(21)—O(6)	123·2 (5)	107·0 (6)
C(12)—C(23)—O(7)	111·1 (5)	112·0 (5)
C(12)—C(23)—O(8)	124·5 (5)	124·3 (6)
O(7)—C(23)—O(8)	124·3 (6)	123·4 (6)
C(17)—O(1)—C(18)	113·4 (4)	116·6 (4)
C(19)—O(3)—C(20)	114·4 (4)	116·4 (3)
C(21)—O(5)—C(22)	116·7 (4)	120·2 (6)
C(23)—O(7)—C(24)	110·8 (5)	115·9 (5)

C(13) which has a torsion angle of −61·4 (1)° and represents a synclinal or *gauche* form of butene. A roughly anticlinal form (torsion angle approximately 108–113°) over this series has been observed for macrocycles having *cis* dienophile geometry.

Earlier communications in which two similar *trans–cis–cis* macrocycles (Michel, Michel-Dewez, Roughton, Springer & Hoogsteen, 1989*a*) were predicted and observed to afford selectively *trans–syn–cis* tricycles (Michel, Michel-Dewez, Roughton, Springer & Hoogsteen, 1989*b*; Michel, Michel-Dewez & Roughton, 1989) provided excellent examples of the transannular Diels-Alder ring construction methodology. Macrocycle (I), however, was predicted through analysis similar to that used for a systematic model study (Lamothe, Ndibwami & Deslongchamps, 1988*b*) to give tricycle (III), but instead gave tricycle (II). The relative stereochemistry of this unexpected adduct (Fig. 2) is *cis* for the *AB* ring junction, *anti* between the C(8) and C(9) protons, and *cis* for the *BC* ring junction. The double bond of the ring *B* half-chair bears the C(15) methyl group extending equatorially out from the molecule. Although the tricycle is, in principle, conformationally mobile due to the *cis–anti–cis* stereochemistry, the C(16) methyl group sits axially on the ring *A* chair conformation; the equatorial methyl conformer is presumably a higher energy form. Ring *C* adopts a normal chair conformation. The two molecules of (II) in the asymmetric unit (Fig. 2) are stereoisomers differing one from the other by conformational changes induced by different orientations of the ester group substituents.

The crystallographic data presented here, and the results of earlier transannular cyclization (Lamothe, Ndibwami & Deslongchamps, 1988*a*) provide a possible explanation for the transformation of (I) to (II).

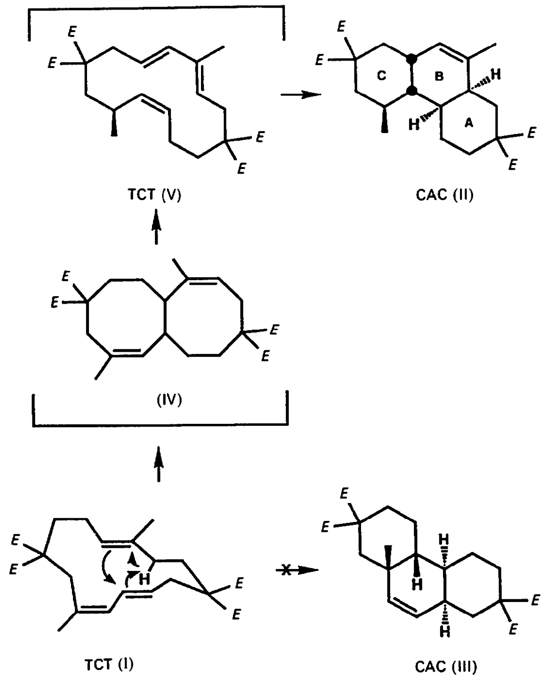

Fig. 1. Molecular schemes, $E = COOCH_3$.

If macrocycle (I) had an inherent preference to conserve the C(2)—C(1)—C(14)—C(13) synclinal form of butene seen here, then an alternate reaction to the Diels–Alder cycloaddition – plagued by considerable steric interactions in the transition state – might become favoured. In this way an ene/retro-ene/Diels–Alder sequence could proceed from (I) *via* a bicyclic intermediate (IV) and a macrocyclic *trans–cis–trans* (*TCT*) triene (V) (Fig. 1) to finally produce the tricyclic (*CAC*) (II) *cis–anti–cis* compound. Both crystal structures constitute a solid structural basis for further speculation on the cycloaddition pathway linking macrocycles to tricycles. No abnormally short intermolecular contacts were noted.

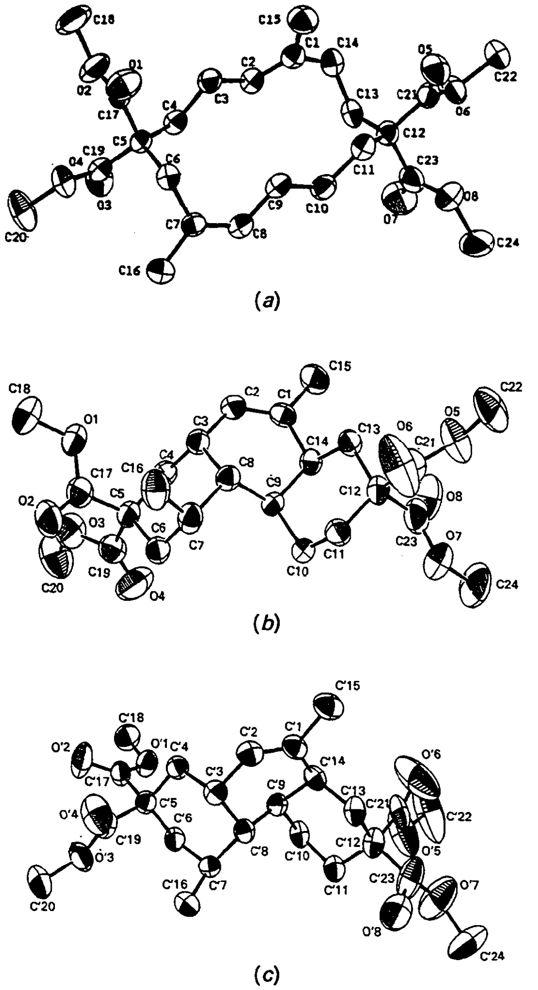

Fig. 2. *ORTEP* (Johnson, 1976) perspective views and atom numbering for both title compounds: (*a*) compound (I), (*b*) compound (II) molecule 1 and (*c*) compound (II) molecule 2.

References

Gabe, E. J., Lee, F. L. & LePage, Y. (1985). *The NRCVAX Crystal Structure System.* In *Crystallographic Computing* 3: *Data Collection, Structure Determination, Proteins, and Databases*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 167–174. Oxford: Clarendon Press.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lamothe, S., Ndibwami, A. & Deslongchamps, P. (1988*a*). *Tetrahedron Lett.* **29**, 1641–1644.

Lamothe, S., Ndibwami, A. & Deslongchamps, P. (1988*b*). *Tetrahedron Lett.* **29**, 1639–1640.

Marinier, A. & Deslongchamps, P. (1988). *Tetrahedron Lett.* **29**, 6215–6219.

Michel, A. G., Boulay, G. & Marinier, A. (1989). *Acta Cryst.* C**45**, 325–327.

Michel, A. G., Michel-Dewez, N. & Roughton, A. L. (1989). *Acta Cryst.* C**45**, 327–329.

Michel, A. G., Michel-Dewez, N., Roughton, A., Springer, J. P. & Hoogsteen, K. (1989*a*). *Acta Cryst.* C**45**, 932–935.

Michel, A. G., Michel-Dewez, N., Roughton, A., Springer, J. P. & Hoogsteen, K. (1989*b*). *Acta Cryst.* C**45**, 909–911.

Michel, A. G., Proulx, M. & Michel-Dewez, N. (1988). *Acta Cryst.* C**44**, 1646–1648.

Roughton, A. (1988). MSc Thesis, Univ. de Sherbrooke, Canada.

Acta Cryst. (1991). C**47**, 1036–1038

Structure of 2-Anilino-4,6-dimethoxy-1,3,5-triazine

By Marek L. Główka and Iwona Iwanicka

Institute of General and Ecological Chemistry, Technical University of Łódź, 90-924 Łódź, Poland

(*Received* 29 *January* 1990; *accepted* 23 *August* 1990)

Abstract. $C_{11}H_{12}N_4O_2$, $M_r = 232{\cdot}2$, monoclinic, $P2_1/c$, $a = 10{\cdot}980\ (1)$, $b = 6{\cdot}317\ (1)$, $c = 16{\cdot}207\ (2)$ Å, $\beta = 90{\cdot}64\ (1)°$, $V = 1124{\cdot}0$ Å^3, $D_x = 1{\cdot}372$ Mg m^{-3}, $Z = 4$, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 0{\cdot}78$ mm^{-1}, $F(000) = 488$, $T = 293$ K, final $R = 0{\cdot}058$ for 1434 observed $[F > 2\sigma(F)]$ reflections. The lengths of the N(amine)—C bonds linking the phenyl and *s*-triazine rings [1·415 (4) and 1·350 (4) Å, respectively] indicate extensive conjugation, as do the C(triazine)—OMe distances [1·342 (4) and 1·329 (3) Å]. The near pla-

0108-2701/91/051036-03$03.00