

mined from electron diffraction is slightly longer but not to a highly significant extent [1.767 (5) Å; Jandal, Seip & Torgrimsen (1976)].

There is some pyramidality at the olefinic C and the donor N atoms. C(2) in (I) deviates from the plane of the bonded atoms by 0.056 (4) Å whereas C(3) is planar. There is no significant pyramidality at the olefinic C atoms in the case of (II). N(3) in (I) deviates from the plane of the bonded atoms by 0.034 (5) Å. In (II), N(3) and N(4) deviate by 0.037 (4) and 0.028 (3) Å respectively from the planes of their bonded atoms. In (I), the NMe₂ group is twisted by 23 (1)° with respect to the least-squares plane defined by N(3), S, C(3) and C(2). In (II), the N(3)Me₂ group is twisted by 32 (1)° whereas the N(4)Me₂ group is twisted by 34 (1)° with respect to the least-squares plane through N(3), N(4), C(3) and C(2).

Figs. 3 and 4 show the packing of the molecules in the unit cells of (I) and (II) respectively.

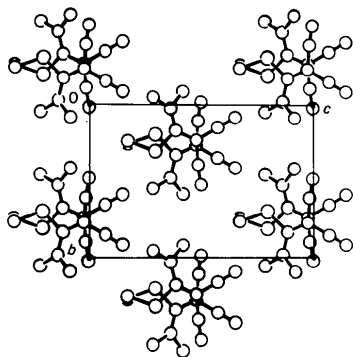


Fig. 3. Packing of the molecules viewed down *a* for (I).

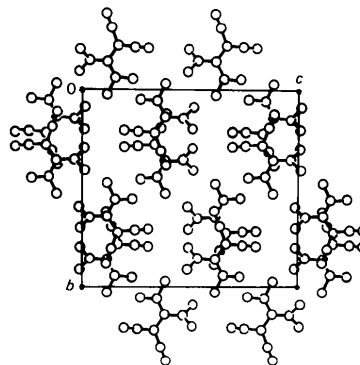


Fig. 4. Packing of the molecules viewed down *a* for (II).

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Structure of Tetramethyl Bicyclo[2.2.2]oct-5-ene-2-endo,3-exo,7-endo,8-exo-tetracarboxylate,† C₁₆H₂₀O₈

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Abstract. *M_r* = 340, monoclinic, *P*2₁/*c*, *a* = 6.080 (2), *b* = 11.468 (4), *c* = 22.901 (5) Å, β = 97.67 (4)°,

V = 1582.5 (9) Å³, *Z* = 4, *D_x* = 1.427 Mg m⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 0.73 mm⁻¹, *F*(000) = 720, *T* = 295 K. The structure was solved by direct methods and refined by full-matrix least squares to a conventional *R* = 0.060 for 1949 observed reflections. The two

† IUPAC name: Tetramethyl (5*R**,6*R**,7*S**,8*S**)-Bicyclo[2.2.2]oct-2-ene-5,6,7,8-tetracarboxylate.

exo methoxycarbonyl substituents are distorted from their axial positions with a mean deviation of 4.0° from the tetrahedral angle and the bicyclic system is slightly twisted from the totally eclipsed conformation.

Introduction. The title compound (hereafter TT') was investigated following our conformational study of rigid molecules with internal strain (Albinati, Brückner & Allegra, 1977; Brückner, Allegra, Albinati & Farina, 1980). TT' was prepared by epimerization of tetramethyl bicyclo[2.2.2]oct-5-ene-2-*endo*,3-*endo*,7-*endo*,8-*endo*-tetracarboxylate in refluxed MeOH in the presence of MeONa. The compound was isolated as crystalline product from the reaction mixture, recrystallized from MeOH (m.p. 421 K) and characterized by ^1H and ^{13}C NMR spectra.

The comparison between thermodynamic parameters of TT' and the more stable TT epimer (two *endo* and two *exo* substituents in a *trans* arrangement) (Grassi, Di Silvestro & Farina, 1981) showed an unexpected small difference of relative internal energy contents: $\Delta G(\text{TT}-\text{TT}') = 1.5 \pm 0.2 \text{ kJ mol}^{-1}$. As a possible explanation, a slight deformation of the TT' molecule was suggested, to move away the substituents in 3,8-*syn*-diaxial positions and reduce their unfavourable interaction. To verify this hypothesis we undertook the X-ray diffractometric analysis reported here.

Experimental. Colourless plate-like crystal, Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$, least-squares fit of 18 reflections to obtain cell dimensions, 2685 independent $\pm h,k,l$ with $2\theta \leq 48^\circ$, 1949 with $I \geq 2\sigma(I)$, $\theta-2\theta$ scan technique, three periodically monitored reflections with no significant intensity variation, Lp correction, absorption ignored; direct methods (MULTAN, Main, Lessinger, Woolfson, Germain & Declercq, 1977), 196 normalized structure factors with $E \geq 1.8$, anisotropic full-matrix refinement, isotropic for H (located from difference map), function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 1.0/[\sigma^2(F_o) + 0.0423(F_o)^2]$, final $R = 0.060$ and $R_w = 0.071$;* scattering factors for C and O from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965).

Discussion. Positional and isotropic thermal parameters are given in Table 1. The molecular structure in the projection giving a good resolution of atoms with bond lengths is shown in Fig. 1. The bond distances are within currently acceptable limits (Yokozeki & Kuchitsu, 1971; Destro, Filippini, Gramaccioli & Simon-

etta, 1969, 1971; Dykes & Davis, 1977), while some significant distortion is detectable in bond angles, as reported in Table 2. The two *exo* substituents, *i.e.* the methoxycarbonyl groups bonded to C(3) and C(8), are expected to undergo rather severe non-bonded interactions with each other; this unfavourable interaction is alleviated by enlarging C(10)-C(3)-C(4), C(3)-C(4)-C(8) and C(4)-C(8)-C(11) bond angles. In fact, these angles are 2.4 , 3.7 and 4.4° respectively greater than the corresponding angles concerning the

Table 1. Atomic fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}^\dagger
O(1)	-1459 (3)	2481 (2)	2383 (1)	3.9 (2)
O(2)	1526 (4)	1707 (4)	2100 (1)	7.0 (3)
O(3)	6785 (4)	621 (2)	3463 (1)	4.3 (2)
O(4)	3435 (4)	254 (2)	3685 (2)	6.1 (3)
O(5)	7050 (4)	2114 (2)	4646 (1)	4.0 (2)
O(6)	3624 (4)	2030 (3)	4876 (1)	5.3 (2)
O(7)	-737 (3)	4963 (2)	4149 (1)	3.5 (2)
O(8)	2763 (4)	5515 (2)	4402 (1)	4.1 (2)
C(1)	1288 (4)	3573 (3)	3301 (1)	2.5 (2)
C(2)	1620 (4)	2317 (3)	3105 (1)	2.5 (2)
C(3)	4127 (5)	2038 (3)	3200 (1)	2.4 (2)
C(4)	5376 (5)	3057 (3)	3529 (2)	2.8 (2)
C(5)	4933 (5)	4086 (3)	3139 (2)	3.0 (2)
C(6)	2799 (5)	4345 (3)	3004 (2)	2.7 (2)
C(7)	1975 (4)	3630 (3)	3969 (1)	2.4 (2)
C(8)	4456 (5)	3331 (3)	4108 (1)	2.6 (2)
C(9)	632 (5)	2121 (3)	2477 (2)	2.9 (2)
C(10)	4654 (5)	879 (3)	3474 (2)	3.0 (2)
C(11)	4912 (6)	2420 (3)	4579 (2)	3.0 (2)
C(12)	1466 (5)	4805 (3)	4203 (1)	2.6 (2)
C(13)	-2623 (7)	2426 (4)	1794 (2)	4.0 (3)
C(14)	7595 (7)	-459 (4)	3720 (2)	5.1 (4)
C(15)	7775 (8)	1309 (4)	5109 (2)	5.4 (4)
C(16)	-1516 (6)	6064 (3)	4326 (2)	3.9 (3)

$$\dagger B_{\text{eq}} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i a_j a_i^* a_j^*$$

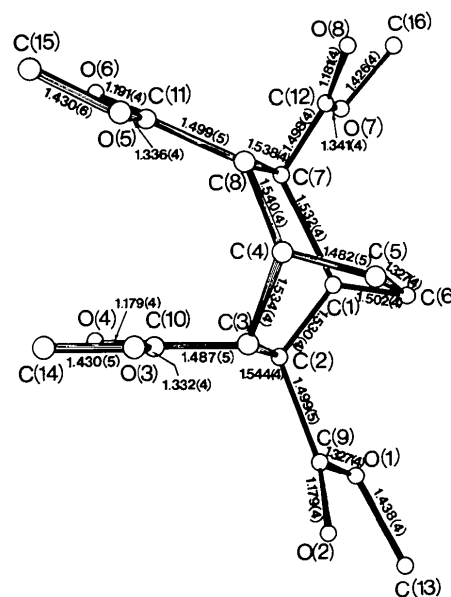


Fig. 1. View of the molecule with the numbering of the atoms and bond distances (\AA).

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38300 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond angles (°) with e.s.d.'s

C(2)—C(1)—C(6)	108.0 (3)	C(4)—C(8)—C(11)	115.1 (3)
C(2)—C(1)—C(7)	107.7 (3)	C(7)—C(8)—C(11)	112.7 (3)
C(6)—C(1)—C(7)	109.0 (3)	C(2)—C(9)—O(1)	111.2 (3)
C(1)—C(2)—C(3)	108.7 (3)	C(2)—C(9)—O(2)	126.7 (3)
C(1)—C(2)—C(9)	111.8 (3)	O(1)—C(9)—O(2)	122.1 (3)
C(3)—C(2)—C(9)	111.4 (2)	C(3)—C(10)—O(3)	110.2 (3)
C(4)—C(3)—C(2)	109.0 (3)	C(3)—C(10)—O(4)	127.2 (3)
C(4)—C(3)—C(10)	114.2 (3)	O(3)—C(10)—O(4)	122.6 (3)
C(2)—C(3)—C(10)	113.4 (3)	C(8)—C(11)—O(5)	110.5 (3)
C(3)—C(4)—C(5)	105.9 (3)	C(8)—C(11)—O(6)	126.9 (4)
C(3)—C(4)—C(8)	111.4 (3)	O(5)—C(11)—O(6)	122.6 (4)
C(5)—C(4)—C(8)	107.4 (3)	C(7)—C(12)—O(7)	109.9 (3)
C(4)—C(5)—C(6)	114.3 (3)	C(7)—C(12)—O(8)	126.8 (3)
C(1)—C(6)—C(5)	113.6 (3)	O(7)—C(12)—O(8)	123.3 (3)
C(1)—C(7)—C(8)	109.1 (2)	C(9)—O(1)—C(13)	118.7 (3)
C(1)—C(7)—C(12)	110.7 (2)	C(10)—O(3)—C(14)	117.8 (3)
C(8)—C(7)—C(12)	111.7 (2)	C(11)—O(5)—C(15)	117.0 (3)
C(4)—C(8)—C(7)	109.0 (2)	C(12)—O(7)—C(16)	117.3 (3)

two *endo* substituents, thus increasing the C(10)···C(11) distance by about 0.6 Å. This effect is coupled with a slight twisting of the bicyclic system from the totally eclipsed conformation around the C(1)—C(4) axis, as described in Table 3. The torsion angles at C(2)—C(3), C(5)—C(6) and C(7)—C(8) are significantly non-zero. In addition, the three cross-ring torsion angles at C(1)···C(4) are evidence for the angular amplitude τ of twisting. A twisting effect has already been observed in a substituted bicyclo[2.2.2]octene (Dykes & Davis, 1977), but in the present case it is perturbed by the contemporary distortion of bond angles at C(4); the net result is a value of τ_3 opposite to those of τ_1 and τ_2 .

Least-squares planes through the region of the molecule which is of particular interest together with interplanar angles are also reported in Table 3. No significant intermolecular contacts are observed in the crystal packing.

Table 3. Conformation of the bicyclo[2.2.2]octene skeleton

(a) Some selected torsion angles

Bond torsion angles (°)	
C(1)—C(2)—C(3)—C(4)	7.1 (3)
C(1)—C(6)—C(5)—C(4)	3.0 (5)
C(1)—C(7)—C(8)—C(4)	-1.0 (3)
O(3)—C(10)—C(3)—C(2)	170.8 (3)
O(5)—C(11)—C(8)—C(7)	174.4 (3)
O(1)—C(9)—C(2)—C(3)	-173.1 (3)
O(7)—C(12)—C(7)—C(8)	-171.1 (3)

Cross-ring torsion angles (°)

$\tau_1 = \text{C}(2)-\text{C}(1)\cdots\text{C}(4)-\text{C}(3)$	4.3 (3)
$\tau_2 = \text{C}(6)-\text{C}(1)\cdots\text{C}(4)-\text{C}(5)$	1.5 (4)
$\tau_3 = \text{C}(7)-\text{C}(1)\cdots\text{C}(4)-\text{C}(8)$	-0.6 (3)

(b) Least-squares planes

Plane	Atoms in plane	Root-mean-square displacement (Å)
I	C(1), C(2), C(3), C(4)	0.033
II	C(1), C(5), C(6), C(4)	0.011
III	C(1), C(7), C(8), C(4)	0.004
Planes	Dihedral angle (°)	
I-II	120.0 (1)	
I-III	118.8 (2)	
II-III	121.1 (2)	

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Détermination Structurale à 163 K du Monomère Bis[*p*-chlorophényl]carbamate] de Hexadiyne-2,4 Diyl-1,6, C₂₀H₁₄Cl₂N₂O₄

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Abstract. $M_r = 417.2$, triclinic, $P\bar{1}$, $a = 12.225$ (3), $b = 8.144$ (4), $c = 4.789$ (3) Å, $\alpha = 100.3$ (3), $\beta = 84.0$ (3), $\gamma = 96.5$ (1)°, $V = 464$ Å³, $Z = 1$, $D_x =$

1.507 Mg m⁻³, $F(000) = 214$, $\lambda(\text{Cu K}\alpha) = 1.54178$ Å, $\mu = 3.45$ mm⁻¹, $T = 163$ K, $R = 0.06$ for 1167 hkl with $F_o \geq 0.008F_{o(\text{max})}$. The monomer crystal presents