DANIELS, P., ERDTMAN, H., NISHIMURA, K., NORIN, T., KIERKEGAARD, P. & PILOTTI, A.-M. (1972). *Chem. Commun.* pp. 246–247.
FARGES, G. & DREIDING, A. S. (1966). *Helv. Chim. Acta*, **49**, 552–561.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.
HASS, B., WILLOUGHBY, T. V., MORIMOTO, C. N., CULLEN, D. L. & MEYER, E. F. JR (1975). *Acta Cryst.* B**31**, 1225–1229.
HOUSTY, J. & CLASTRE, J. (1957). *Acta Cryst.* **10**, 695–698.
HUDSON, J. A. & HEDGES, R. M. (1969). *Molecular Luminescence*, edited by E. C. LIM. New York: Benjamin.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794, revised.
KELLER, R. A. (1968). *J. Amer. Chem. Soc.* **90**, 1940–1944.
KITAIGORODSKII, A. I. (1955). *Organic Chemical Crystallography*. New York: Consultants Bureau.
KLUNK, D. G. & MEYER, E. F. JR (1974). *Nature, Lond.* **248**, 761–762.
KOYAMA, H. & IRIE, T. (1972). *J. Chem. Soc. Perkin* II, pp. 351–353.
MARIEZCURRENA, R. A., RASMUSSEN, S. E., LAM, J. & WOLLENWEBER, E. (1972). *Tetrahedron Lett.* **30**, 3091–3092.
MEYER, E. F. JR (1973). *J. Appl. Cryst.* **6**, 45.
NEWMAN, M. S. (1972). *Acc. Chem. Res.* **5**, 354–360.
PILOTTI, A. (1972). *Acta Cryst.* B**28**, 2123–2128.
SCHENK, H. (1972). *Acta Cryst.* B**28**, 625–628.
SIMMONS, H. E. & FUKUNAGA, T. (1967). *J. Amer. Chem. Soc.* **89**, 5208–5215.
SLETTEN, E., SLETTEN, J. & JENSEN, L. H. (1969). *Acta Cryst.* B**25**, 1330–1338.
SPARKS, R. (1974). *Computers in Chemistry and Industry*, Vol. 5. New York: Marcel Dekker.
WARD, R. S. (1973). *Chem. Brit.* **9**, 444–449, 465.
WEBER, H. P. & GALANTAY, E. (1972). *Helv. Chim. Acta*, **55**, 544–553.
WILLIAMS, D. E. (1969). *Acta Cryst.* A**25**, 464–470.
WILLIAMS, D. E. (1972). *Acta Cryst.* A**28**, 629–635.
WILLIAMS, D. E. (1973*a*). *Acta Cryst.* B**29**, 96–102.
WILLIAMS, D. E. (1973*b*). Personal communication.
WILLOUGHBY, T. V., MORIMOTO, C. N., SPARKS, R. A. & MEYER, E. F. JR (1974). *J. Appl. Cryst.* **7**, 430–434.
ZUGENMAIER, P. & SARKO, A. (1972). *Acta Cryst.* B**28**, 3158–3166.

Acta Cryst. (1976). B**32**, 561

The Synthesis and Molecular Structure of a Cage Dimer of 7-t-Butoxynorbornadiene

BY S. C. NEELY, DICK VAN DER HELM,* ALAN P. MARCHAND AND B. R. HAYES
University of Oklahoma, Norman, Oklahoma 73069, *U.S.A.*

(*Received* 8 *May* 1975; *accepted* 1 *July* 1975)

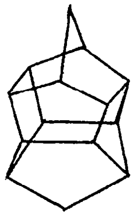
The cage dimer, 13,14-di-t-butoxyheptacyclo$[5,5,1,1^{4,10},0^{2,6},0^{3,11},0^{5,9},0^{8,12}]$tetradecane is obtained as one of the products in the thermal reaction of 7-t-butoxynorbornadiene with iron pentacarbonyl. The preparation, purification and spectral data of the compound are described. Crystals of the dimer are triclinic, space group $P\bar{1}$. The cell dimensions are $a=6{\cdot}282$ (1), $b=11{\cdot}159$ (2), $c=14{\cdot}219$ (3) Å, $\alpha=106{\cdot}49$ (2)°, $\beta=92{\cdot}66$ (2)° and $\gamma=97{\cdot}17$ (2)°. The structure was determined by direct methods and refined with least-squares calculations using 3220 data. The final R value is 0·081. Both the distances of like bonds and the values of corresponding bond angles are closely similar. The longest bond distances 1·568 (4) Å are the four ethano bridges of the norbornane systems. All other bond distances in the cage are between 1·526 and 1·544 Å. The results on the cage dimer are generally in good agreement with the electron diffraction results of Dallinga & Toneman [*Rec. Trav. Chim. Pays-Bas* (1968), **87**, 795–804]. The major difference is a change in the flap angle, which, however, does not change the conformation of the five-membered rings of the norbonane skeleton.

Introduction

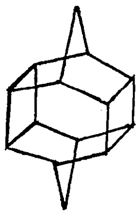
The reaction of norbornadiene (1) with iron carbonyls has been extensively studied (Bird, 1962, 1967). Of particular interest is a saturated dimeric species [(2) $C_{14}H_{16}$] formed in the photochemical reaction of (1) with iron pentacarbonyl (Lemal & Shim, 1961) and in the thermal reaction of (1) with diiron enneacarbonyl (Bird, Colinese, Cookson, Hudec & Williams, 1961). Structures (2*a*) and (2*b*) have been suggested for this saturated dimer. More recently, indirect chemical evidence has been forwarded which supports structure (2*a*) [rather than (2*b*)] for this dimer (Acton, Roth, Katz, Frank, Maier & Paul, 1972). However, to our knowledge, no direct method (X-ray crystallography, electron or neutron diffraction) has been applied to verify this structural assignment.

---

* Supported in part by N.H.I. Development Award K4-GM-42, 572.

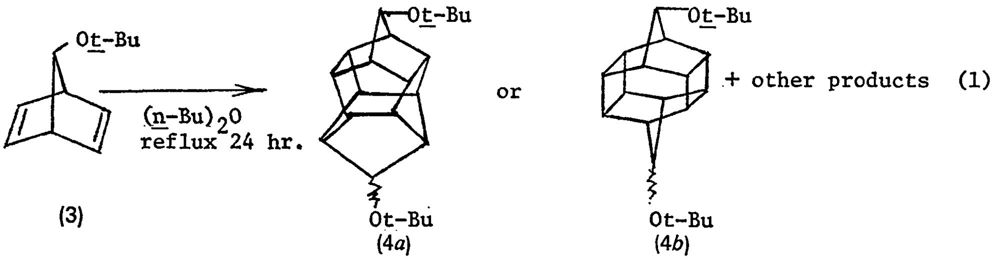


(2*a*)



(2*b*)

In the present study, the thermal reaction of 7-t-butoxynorbornadiene (3) with iron pentacarbonyl has likewise been found to afford a saturated cage dimer (4) (along with other products). The molecular formula of (4) was established as $C_{22}H_{32}O_2$ *via* its mass spectrum and *via* elemental microanalysis (see *Experimental*). However, as was previously the case with (2*a*) *vs.* (2*b*), conventional spectroscopic techniques (n.m.r., infrared, and mass spectra) did not permit a clear distinction to be made between (4*a*) and (4*b*) as possible structures for the $C_{22}H_{32}O_2$ cage dimer formed in the reaction shown in the following scheme:



Accordingly, we turned to single-crystal X-ray diffraction analysis in an effort to provide conclusive proof for the structure of (4).

Experimental

Synthesis

To a solution of (3) (10·0 g, 61·0 mmol) in di-n-butyl ether (75 ml) was added iron pentacarbonyl (25·00 g, 127·5 mmol). The resulting solution was refluxed with stirring for 24 h. During the reflux period, a slow stream of dry nitrogen was swept through the reaction mixture. At the conclusion of the reflux period, the hot reaction mixture was filtered through a bed of Celite, and the filtrate was concentrated on a rotary evaporator. The concentrate was stirred with an acetone solution of ferric chloride (excess) for 20 h to destroy any organoiron carbonyl complexes present (Shvo & Hazum, 1974). The resulting solution was then poured into water (500 ml) and extracted three times with 50 ml portions of hexane. The hexane extracts were combined, dried (anhydrous sodium sulfate), filtered, and then concentrated, affording a viscous brown oil (4·40 g). The oil was purified by elution chromatography on t.l.c. grade silica gel (100 g, manufactured by E. Merck A. G., Darmstadt, W. Germany, column dimensions 4 × 50 cm, 1:9 ethyl acetate–hexane eluant). The first fraction thereby obtained afforded a colorless, viscous oil (600 mg, 5·53%). The oil was taken up in pentane and recrystallized (−78°) to afford colorless needles (470 mg), m.p. 131–132°. N.m.r. spectrum: δ 1·18 [s, 18H, $OC(CH_3)_3$], δ 2·33 (mult, 8H, methine C–*H*), δ 2·76 (mult, 4H, norbornyl ring bridgehead protons), δ 4·28 (mult, 2H, $>$CH–Ot–Bu); infrared spectrum: 2970 (*s*), 1455 (*w*), 1385 (*m*), 1360 (*m*), 1292 (*w*), 1245 (*m*), 1225 (*m*), 1195 (*s*), 1085 (*s*), 1055 (*m*) 920 (*w*), 887 cm^{-1} (*w*); mass spectrum, m/e (% of base peak): 328 (parent ion, 16%), 314 (34), 313 (84), 255 (66), 200 (44), 199 (100), 187 (49), 91 (39), 79 (31), 57 (73), 41 (42).

Melting points are uncorrected. N.m.r. spectra were obtained on a Varian XL-100-15 spectrometer ($CDCl_3$ solvent, TMS internal standard). Infrared spectra were obtained on a Beckmann IR-8 infrared spectrophotometer (CCl_4 solution), mass spectra were obtained at 70 eV on a Hitachi–Perkin Elmer RMU 7E mass spectrometer.

Analysis calculated for $C_{22}H_{32}O_2$: C, 80·49; H, 9·76%. Found (Chemalytics, Inc.): C, 80·37; H, 9·91%.

Crystallographic data

Crystals were obtained by recrystallization from pentane at 0°C; the dimensions of the data crystal were 0·33 × 0·05 × 0·11 mm and showed a mosaic spread of less than 0·5°. The symmetry of the intensity data showed the crystal system to be triclinic and the structure determination proved the space group to be $P\bar{1}$. The 3220 data, comprising all unique reflections with 2θ less than 130°, were collected using Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) on a Nonius CAD-4 automatic diffractometer. The integrated intensity data were collected with θ–2θ scans in which the θ-scan width was

Table 1. *Crystallographic data*

$C_{22}H_{32}O_2$
Space group: $P\bar{1}$
$a =$ 6·282 (1) Å
$b =$ 11·159 (2)
$c =$ 14·219 (3)

$\alpha = 106{\cdot}49$ (2)°
$\beta =$ 92·66 (2)
$\gamma =$ 97·17 (2)

F.W. 328·50
$V = 944{\cdot}7$ Å^3
$Z = 2$
$D_c = 1{\cdot}155$ g cm^{-3}
$D_o = 1{\cdot}174$ (measured by flotation in aq. Na_2SO_4)
$F(000) = 360$

between 1·0° and 1·2°. Maximum scan time was 120 s, $\frac{2}{3}$ of the time being spent scanning the peak and $\frac{1}{6}$ of the time on each the left and right background. The crystallographic data are summarized in Table 1. Least-squares cell dimensions were computed from averages of $+2\theta$ and -2θ values of 29 reflections.

Of the 3220 reflections, 871 were not distinct from background as judged by the fact that the net count of these peaks was less than $2T^{1/2}$. Here T is the sum of the peak count plus twice the left and right background counts. For the purpose of least-squares refinement, these 871 intensities were assigned values of $1{\cdot}16T^{1/2}$. Lorentz and polarization measurements were applied to the data. Absorption corrections were not necessary since the linear absorption coefficient, μ, was only 5·61 cm^{-1}. Each structure amplitude was assigned a weight factor given by $w_F = 1/\sigma_F^2$ where the standard deviation (σ_F) of the amplitude is given by

$$\sigma_F = \tfrac{1}{2}\left[\frac{\sigma^2 + (0{\cdot}06P)^2}{\text{Lp}\,.\,P}\right]^{1/2}$$

in which $\sigma = T^{1/2}V$, V=scan speed, $P = [\text{Pk} - 2(R + L)]V$, Pk = peak count, R = right background count, L = left background count, Lp = Lorentz–polarization factor.

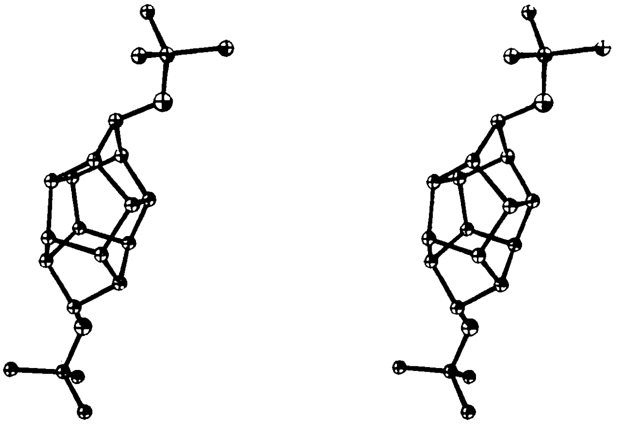


Fig. 1. Stereo view of the molecule generated by the *ORTEP* program (Johnson, 1965).

Structure determination and refinement

The structure was solved by direct methods (Karle & Karle, 1966) using the symbolic addition programs of Hall & Ahmed, 1968. The distribution and statistics of $|E|$ indicated a centrosymmetric space group (Karle, Dragonette & Brenner, 1965). The $3,\bar{4},10$, $\bar{5}43$, and $4\bar{3}9$ reflections were used to fix the origin. 390 signed reflections with E values over 1·50 were used to calculate an E map in which all C and O atoms were readily identifiable. These 24 atomic positions were refined initially with isotropic temperature factors. In later cycles anisotropic temperature factors were used.

The 32 H atoms were located from a difference Fourier synthesis. The parameters of the H atoms of the cage system were refined with isotropic temperature factors. However, to limit the number of parameters, the coordinates of the t-butoxy H atoms were not refined. No disorder was indicated.

The least-squares refinement, using the block-diagonal method, converged to a value for $R(=\sum||kF_o| - |F_c||/\sum|kF_o|)$ of 0·081. The quantity minimized in the least-squares calculations was $\sum w_F(|kF_o| - |F_c|)^2$. The 871 reflections, which could not be distinguished from

Table 2. *Atomic fractional coordinates and thermal parameters of carbon and oxygen atoms*

The temperature factor is expressed as $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})$. Standard deviation for last digit is in parentheses. All parameters are multiplied by 10^4.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
C(1)	3181 (4)	1969 (2)	−1165 (2)	240 (7)	76 (2)	37 (1)	26 (3)	41 (5)	73 (6)
C(2)	2320 (4)	1194 (2)	−491 (2)	286 (8)	63 (2)	41 (1)	27 (3)	4 (5)	50 (7)
C(3)	3793 (4)	1628 (2)	466 (2)	223 (7)	65 (2)	45 (1)	38 (3)	10 (5)	85 (6)
C(4)	2351 (4)	1849 (2)	1321 (2)	200 (6)	80 (2)	42 (1)	59 (3)	6 (5)	27 (6)
C(5)	539 (4)	2409 (2)	899 (2)	175 (6)	102 (3)	40 (1)	57 (3)	22 (5)	44 (6)
C(6)	147 (4)	1711 (2)	−204 (2)	189 (7)	92 (3)	44 (1)	61 (3)	−18 (5)	−29 (6)
C(7)	68 (4)	2713 (2)	−751 (2)	173 (6)	94 (2)	42 (1)	52 (3)	−4 (5)	37 (6)
C(8)	1787 (4)	3768 (2)	−116 (2)	203 (6)	63 (2)	40 (1)	39 (3)	5 (4)	72 (6)
C(9)	1617 (4)	3774 (2)	960 (2)	213 (7)	83 (2)	39 (1)	36 (3)	14 (5)	108 (6)
C(10)	3916 (4)	3824 (2)	1419 (2)	208 (6)	70 (2)	37 (1)	30 (3)	−13 (4)	38 (6)
C(11)	4879 (3)	2997 (2)	529 (2)	146 (6)	79 (2)	43 (1)	46 (3)	11 (4)	46 (6)
C(12)	3943 (3)	3253 (2)	−404 (2)	160 (6)	78 (2)	39 (1)	50 (3)	20 (4)	27 (6)
C(13)	1140 (4)	2161 (2)	−1695 (2)	271 (7)	78 (2)	36 (1)	40 (3)	−13 (5)	−1 (7)
C(14)	3604 (4)	2992 (2)	2105 (2)	191 (6)	91 (2)	37 (1)	42 (3)	8 (4)	75 (6)
O(15)	5641 (3)	2797 (2)	2467 (1)	197 (5)	120 (2)	39 (1)	71 (2)	−3 (3)	68 (5)
C(16)	5790 (4)	2376 (2)	3329 (2)	268 (5)	104 (3)	40 (1)	65 (3)	2 (5)	71 (7)
C(17)	4314 (6)	1151 (3)	3226 (3)	528 (14)	133 (4)	99 (3)	151 (5)	−55 (10)	−3 (12)
C(18)	5273 (6)	3388 (3)	4215 (2)	610 (15)	173 (4)	41 (2)	60 (4)	38 (8)	173 (13)
C(19)	8122 (5)	2192 (4)	3433 (3)	332 (10)	267 (6)	83 (2)	186 (6)	13 (8)	229 (13)
O(20)	1582 (3)	3026 (2)	−2250 (1)	341 (6)	101 (2)	36 (1)	57 (2)	−39 (4)	−55 (5)
C(21)	488 (5)	2727 (3)	−3212 (2)	330 (9)	116 (3)	38 (1)	54 (3)	−36 (6)	27 (8)
C(22)	−1928 (5)	2588 (4)	−3155 (3)	338 (11)	230 (6)	99 (3)	177 (7)	−87 (9)	5 (13)
C(23)	1191 (7)	1562 (3)	−3886 (2)	825 (20)	158 (4)	45 (2)	30 (5)	24 (9)	253 (15)
C(24)	1244 (6)	3879 (3)	−3540 (2)	566 (14)	154 (4)	59 (2)	118 (5)	−63 (8)	−58 (12)

the background, were only included in the least-squares calculations when $|F_c| > 2|F_o|$. In the last cycle of refinement this was the case for only 2 of the 871 reflections. All 3220 data were used in the calculation of the standard deviations of the parameters and in the calculation of the standard deviation of an observation of unit weight, which was 1·44. The average values of $w_F \Delta F^2$ did not vary significantly with either F_o or $\sin\theta/\lambda$, validating the weighting scheme used in the refinement. For the final cycle of refinement, all parameter shifts were less than $0{\cdot}2\sigma$. A final difference Fourier map revealed no peaks greater than 0·25 e Å^{-3}.

The atomic scattering factors of C and O were taken from *International Tables for X-ray Crystallography* (1962) while those for H were from Stewart, Davidson & Simpson (1965).

The final atomic parameters are presented in Tables 2 and 3.*

Description and discussion of the structure

A stereo view of the molecule, shown in Fig. 1, verifies that it is 13,14-di-t-butoxy$[5,5,1,1^{4,10},0^{2,6},0^{3,11},0^{5,9},$-

Table 3. *Hydrogen atom parameters*

The positional coordinates are multiplied by 10^3. The hydrogen atoms on the t-butyl groups were not refined.

	x	y	z	B (Å^2)
H(C1)	432 (4)	162 (2)	−160 (2)	3·9 (5)
H(C2)	226 (4)	28 (2)	−79 (2)	4·5 (6)
H(C3)	486 (4)	106 (2)	50 (2)	3·5 (5)
H(C4)	185 (3)	108 (2)	154 (2)	3·4 (5)
H(C5)	−80 (4)	236 (2)	127 (2)	5·7 (7)
H(C6)	−111 (4)	105 (2)	−36 (2)	4·1 (5)
H(C7)	−134 (4)	301 (2)	−84 (2)	4·9 (6)
H(C8)	166 (3)	457 (2)	−22 (2)	3·1 (5)
H(C9)	83 (3)	445 (2)	138 (2)	3·2 (5)
H(C10)	474 (4)	466 (2)	171 (2)	4·1 (5)
H(C11)	645 (4)	303 (2)	61 (2)	4·0 (5)
H(C12)	490 (3)	379 (2)	−67 (2)	3·0 (5)
H(C13)	28 (3)	132 (2)	−217 (2)	2·9 (5)
H(C14)	275 (4)	336 (2)	265 (2)	3·6 (5)
H(C17)1	250	120	320	7·0
H(C17)2	500	50	250	7·0
H(C17)3	450	50	360	7·0
H(C18)1	550	330	480	7·0
H(C18)2	350	350	420	7·0
H(C18)3	620	420	420	7·0
H(C19)1	850	180	400	7·0
H(C19)2	900	320	360	7·0
H(C19)3	850	150	280	7·0
H(C22)1	−250	200	−280	7·0
H(C22)2	−250	250	−380	7·0
H(C22)3	−250	360	−260	7·0
H(C23)1	50	150	−460	7·0
H(C23)2	100	80	−360	7·0
H(C23)3	300	160	−360	7·0
H(C24)1	50	380	−420	7·0
H(C24)2	300	400	−340	7·0
H(C24)3	100	480	−300	7·0

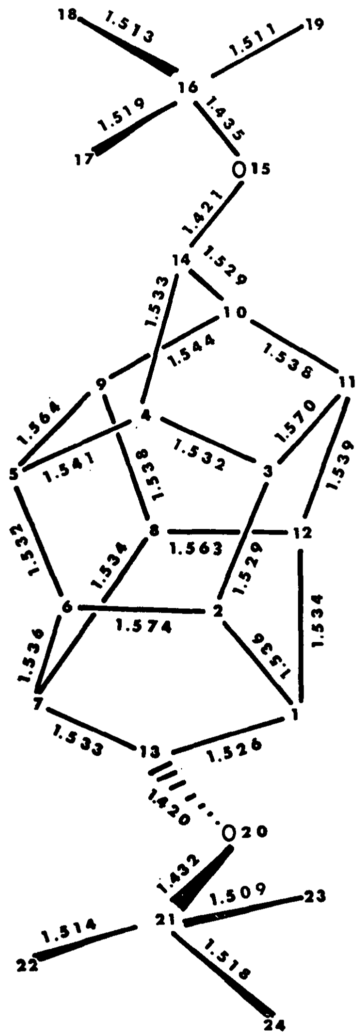


Fig. 2. Bond distances and the numbering scheme. The standard deviations for the bonds shown are 0·003 Å except for the t-butyl C–C distances for which they are 0·004 Å for the bonds to C(17), C(18), C(19) and C(22) and 0·005 Å for bonds to C(23) and C(24).

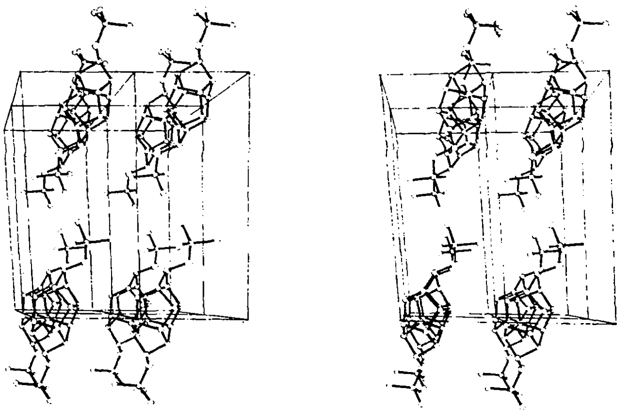


Fig. 3. Stereo view of the crystal packing viewed down the c axis.

---

* The final F table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31234 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

$0^{8,12}$]-tetradecane (4*a*). It consists of a cage of eight five-membered rings, four of which are formed by the cross-dimerization of the two norbornane moieties. The t-butoxy groups are attached to the C(13) and C(14) methylene bridges, and the alkoxy groups are in staggered conformations.

The bond lengths and numbering scheme are shown in Fig. 2. The bond angles are given in Table 4. There is close agreement among equivalent bonds and bond angles, which are grouped accordingly in Tables 4 and 5.

Some of the bond distances in the structure can be compared with similar ones in norbornane. Three different electron diffraction studies on norbornane were published in 1967 and 1968. The results showed large variations. Chiang, Wilcox & Bauer (1968) showed all three types of bond distances to be quite similar, ranging from 1·551 to 1·559 Å. Morino, Kuchitsu & Yokozeki (1967) found the distances in the methylene bridge to be long: 1·568 (18) Å, and the other two types to be the same [1·539 (20) Å]. However, Dallinga & Toneman (1968) pointed out the inherent difficulties in the interpretation of the electron diffraction data of norbornane. They observed the ethano bridge distances to be long [1·578 (18) Å]. Our observations on the corresponding bond distances in the present compound [1·568 (4) Å, type II, Table 5] are in agreement with their observations in norbornane. The same authors found the other two types, *i.e.* the methylene bridge bonds and the bonds leading to the ethano bridges, to be essentially the same (1·534–1·535 Å, with standard deviations between 0·014 and 0·035 Å). Again, our observations (bond types III and IV, Table 5) in (4*a*) are in agreement with these results. The comparison cannot be a direct one, however, because of the differences in strain between the monomer (norbornane) and the cage dimer. Nevertheless, it is worthwhile to point out that, in addition to the agreement noted above, the experimental results of Dallinga & Toneman (1968), for norbornane, agree with results of their own theoretical calculations as well as with the results of Allinger calculations performed by Altona & Sundaralingam (1970).

The bond angles inside the cage can be grouped even more clearly than the bond distances. The standard deviations of the averages of bond-angle measurements are only slightly larger than those for the independent measurements. On comparing the bond angles in (4*a*) (Table 4) with the corresponding bond angles in norbornane (Dallinga & Toneman, 1968), one observes no change in either the methylene bridge angles (95·3 and 95·15°) or the angles involving the ethano bridge C atoms (103·0° for both). However, a large change occurs in what is sometimes called the flap angle [bond angles of the type C(3)–C(4)–C(5)]. In norbornane, the flap angle is 107·1°, whereas we observe a value of 100·4° for the corresponding angle in (4*a*). In addition, we note that the bond angles of the type C(14)–C(4)–C(5) are concomitantly larger in (4*a*) (103·8°) than in norbornane (101·8°).

The worst agreement among equivalent bond angles is for those involving the t-butoxy groups, which is most likely caused by intermolecular interactions (Fig. 3). It is interesting to note that there is a systematic difference between the C–O distances involving the C atoms of the cage and those involving the C atoms of the t-butoxy groups, the former being 0·013 Å shorter than the latter. This is probably caused by the non-ideal sp^3 hybridization of the C(14) and C(13) atoms which results from the very small methylene bridge angles. Accordingly the exocyclic cage bonds possess a relatively high percentage of *s*-character which re-

Table 4. *Bond angles* (°)

Standard deviation for angles in the cage is 0·2°, and in the t-butyl groups 0·3°.

C(4)—C(14)-C(10)	95·2	C(9)—C(8)—C(12)	105·2
C(1)—C(13)-C(7)	95·1	C(8)—C(12)-C(11)	104·9
		C(2)—C(6)—C(5)	104·8
C(3)—C(4)—C(5)	100·4	C(3)—C(2)—C(6)	105·0
C(9)—C(10)-C(11)	100·1	C(5)—C(9)—C(8)	104·9
C(6)—C(7)—C(8)	100·6	C(6)—C(5)—C(9)	105·2
C(2)—C(1)—C(12)	100·5	C(2)—C(3)—C(11)	105·1
average	100·4 (2)	C(3)—C(11)-C(12)	104·8
		average	105·0 (2)
C(4)—C(5)—C(9)	103·4		
C(5)—C(9)—C(10)	102·7	C(5)—C(6)—C(7)	107·4
C(3)—C(11)-C(10)	102·8	C(7)—C(8)—C(9)	107·3
C(4)—C(3)—C(11)	103·2	C(8)—C(9)—C(10)	107·6
C(2)—C(6)—C(7)	102·9	C(10)-C(11)-C(12)	107·9
C(1)—C(2)—C(6)	102·8	C(1)—C(12)-C(11)	107·4
C(1)—C(12)-C(8)	103·0	C(1)—C(2)—C(3)	107·7
C(7)—C(8)—C(12)	103·1	C(2)—C(3)—C(4)	107·5
average	103·0 (2)	C(4)—C(5)—C(6)	107·2
		average	107·5 (2)
C(5)—C(4)—C(14)	103·4		
C(9)—C(10)-C(14)	103·9	C(14)-O(15)-O(16)	119·4
C(11)-C(10)-C(14)	104·0	C(13)-O(20)-C(21)	117·9
C(3)—C(4)—C(14)	103·8		
C(8)—C(7)—C(13)	104·3	C(4)—C(14)-O(15)	114·9
C(12)-C(1)—C(13)	104·4	C(10)-C(14)-O(15)	109·9
C(6)—C(7)—C(13)	103·2	C(7)—C(13)-O(20)	113·4
C(2)—C(1)—C(13)	103·4	C(1)—C(13)-O(20)	111·9
average	103·8 (4)	average	112·5 (18)
O(15)-C(16)-C(17)	112·9	O(20)-C(21)-C(22)	110·6
O(15)-C(16)-C(18)	109·9	O(20)-C(21)-C(23)	110·3
O(15)-C(16)-C(19)	103·7	O(20)-C(21)-C(24)	102·8
C(17)-C(16)-C(18)	109·4	C(22)-C(21)-C(23)	112·3
C(17)-C(16)-C(19)	110·6	C(22)-C(21)-C(24)	110·1
C(18)-C(16)-C(19)	110·3	C(23)-C(21)-C(24)	110·4

Table 5. *Average values of equivalent bond lengths*

I	C(2)-C(3), C(5)-C(6), C(8)-C(9), C(11)-C(12)	1·535 (4)
II	C(2)-C(6), C(8)-C(12), C(3)-C(11), C(5)-C(9)	1·568 (4)
III	C(1)-C(13), C(7)-C(13), C(4)-C(14), C(10)-C(14)	1·530 (3)
IV	C(1)-C(2), C(1)-C(12), C(6)-C(7), C(7)-C(8), C(3)-C(4), C(4)-C(5), C(9)-C(10), C(10)-C(11)	1·537 (4)

Table 6. *Conformational angles in five-membered rings*

a	*b*	*c*	*d*	*e*	*b–c*	*c–d*	*d–e*	*e–a*	*a–b*	Δ†	φ_m†
C(3)	C(4)	C(14)	C(10)	C(11)	52·1	−51·9	32·9	0·2	−33·2	35·6	55·5
C(9)	C(10)	C(14)	C(4)	C(5)	52·3	−52·4	33·4	−0·4	−33·0	36·6	55·8
C(2)	C(1)	C(13)	C(7)	C(6)	53·5	−53·4	33·8	−0·1	−33·8	36·1	56·8
C(8)	C(7)	C(13)	C(1)	C(12)	51·3	−51·5	32·9	−0·1	−32·6	36·4	54·9
C(6)	C(5)	C(4)	C(3)	C(2)	37·3	−37·2	23·6	0·2	−23·7	35·7	39·7
C(11)	C(12)	C(1)	C(2)	C(3)	36·5	−36·6	23·1	0·0	−23·2	36·0	38·9
C(12)	C(11)	C(10)	C(9)	C(8)	36·2	−36·1	23·1	0·0	−23·2	35·9	38·7
C(5)	C(6)	C(7)	C(8)	C(9)	36·5	−36·7	23·5	−0·3	−23·0	36·9	39·0
Norbornane*					55·2	−55·2	34·6	0	−34·6	36	58

* Calculated from the results of Dallinga & Toneman (1968).
† Estimated error in Δ and φ_m's 0·8°.

sults in a corresponding shortening of these bonds. This interpretation is supported by the structure of another product of the reaction of iron pentacarbonyl with 7-t-butoxynorbornadiene [*i.e.*, 1,4,4aα,4bβ,5,8aα,-9aα-octahydro-*anti*,*anti*-10,11-di-t-butoxy-1,4,5,8-dimethanofluoren-9-one(5) (Ealick & van der Helm, 1975)]. The differences between the exocyclic C–O and t-butoxy C–O bond distances in (5) are even larger (0·030 Å) than in (4*a*). We note also that the methylene bridge bond angles in (5) (93·75°) are smaller than the corresponding angles in (4*a*) (95·15°). These results, then, are in accord with the expectations based upon the anticipated non-ideal sp^3 hybridization of the bridge C atoms.

An analysis of the conformations of the eight five-membered rings is given in Table 6. We use the formalism proposed by Altona, Geise & Romers (1968). The phase angle (Δ) is close to 36° for all eight rings, indicating that they are all in the ideal envelope conformation. The maximum amplitudes of torsion, however, differ. Accordingly, the rings can be separated into two groups. For the four non-norbornyl rings forming the band of the cage in (4*a*) φ_m is between 38·7–39·7°. The value of φ_m is between 54·9–56·8° for the four rings of the norbornane moieties in (4*a*). The last values, however, are still quite similar to the value of 58° calculated for norbornane from the results of Dallinga & Toneman (1968).

These last results lead us to conclude that a major change in the flap angle has little or no effect on the conformation of the five-membered rings in the norbornane skeleton. Assuming that the results of Dallinga & Toneman on norbornane are correct, we also conclude that there is a close congruence between the degree of strain in (4*a*) and in norbornane as indicated by the similarities between corresponding bond distances, bond angles and ring conformations in both structures.

A.P.M. gratefully acknowledges support of this study by the University of Oklahoma Research Council. We also thank the University for providing computer facilities.

References

Acton, N., Roth, R. J., Katz, T. J., Frank, J. K., Maier, C. A. & Paul, I. C. (1972). *J. Amer. Chem. Soc.* **94**, 5446–5456.

Altona, C., Geise, H. J. & Romers, C. (1968). *Tetrahedron*, **24**, 13–32.

Altona, C. & Sundaralingam, M. (1970). *J. Amer. Chem. Soc.* **92**, 1995–1999.

Bird, C. W. (1962). *Chem. Rev.* **62**, 283–302.

Bird, C. W. (1967). *Transition Metal Intermediates in Organic Synthesis*, pp. 209–210, and references cited therein. London: Logos Press,

Bird, C W., Colinese, D. L., Cookson, R. C., Hudec, J. & Williams, R. O. (1961). *Tetrahedron Lett.* pp. 373–375.

Chiang, J. F., Wilcox, C. F. Jr & Bauer, S. H. (1968). *J. Amer. Chem. Soc.* **90**, 3149–3157.

Dallinga, G. & Toneman, L. H. (1968). *Rec. Trav. Chim. Pays-Bas*, **87**, 795–804.

Ealick, S. E. & van der Helm, D. (1975). *Cryst. Struct. Commun.* **4**, 369.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202, 214. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.

Karle, I. L., Dragonette, K. S. & Brenner, S. A. (1965). *Acta Cryst.* **19**, 713–716.

Karle, J. & Karle, I. L. (1966). *Acta Cryst.* **21**, 849–859.

Lemal, D. M. & Shim, K. S. (1961). *Tetrahedron Lett.* pp. 368–372.

Morino, Y., Kuchitsu, K. & Yokozeki, A. (1967). *Bull. Chem. Soc. Japan*, **40**, 1552.

Shvo, Y. & Hazum, E. (1974). *Chem. Commun.*pp. 336–337.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.