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The Structure of 3,4:7,8-Dibenzotricyclo[4.2.0.0^{2,5}]octa-3,7-diene

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The structure of 3,4:7,8-dibenzotricyclo[4.2.0.0^{2,5}]octa-3,7-diene has been studied by single-crystal diffraction techniques. This compound (C₁₆H₁₂) crystallizes in the monoclinic space group *P*2₁/*c*, with *a* = 10·716, *b* = 7·706, *c* = 6·719 Å, β = 98·37°, *Z* = 2. The structure was determined by the symbolic addition procedure and was refined by block-diagonal least squares methods to a final *R* value of 0·069, including hydrogen atoms. The molecule is in the *anti* configuration, with two planar benzocyclobutene systems on opposite sides of a planar central cyclobutane ring. The bridgehead bond, common to two four-membered rings, is found to be unusually long, 1·593 Å.

Introduction

Since the early fifties, transition metal complexes and complex intermediates have become widely used for producing many organic compounds which would have been difficult or impossible to make otherwise. In producing benzocyclobutadiene and cyclobutadiene (Emerson, Watts & Pettit, 1965) by such methods many new and interesting compounds have been isolated. Three dimers of benzocyclobutadiene have been so prepared (Emerson *et al.*, 1965; Avram, Dinu & Nenitescu, 1959; Cava & Napier, 1957). Formation of these dimeric products of benzocyclobutadiene is dependent upon different transition metals which act as catalysts. The title compound, hereinafter referred to as DBTCO, is the one of these dimers which was prepared using nickel tetracarbonyl as a catalyst (Avram *et al.*, 1959; Cava & Napier, 1957). This compound has so far only been isolated in one configuration, which has been shown by Griffin & Weber (1961) to be *anti*.

In other systems containing four-membered rings, the ring is in either the planar or the puckered conformation, and often exhibits unusually long carbon-carbon bond distances (Adman & Margulis, 1968). Fusion of other rings to four-membered rings seems to have varying effects on the cyclobutane ring geometry, depending on the nature of the fusing rings (Margulis, 1965; Einstein, Hosszu, Longworth, Rahn & Wei, 1967; Adman, Gordon & Jensen, 1968; Camerman, Weinblum & Nyburg, 1969; Camerman & Nyburg, 1969; Barnett & Davis, 1970). The present investigation was undertaken to determine the effect on ring

geometry of fusion of cyclobutane with two highly strained four-membered rings.

Experimental

Suitable crystals for X-ray studies were obtained by recrystallization of a sample of DBTCO, kindly supplied by Professor R. Pettit, from an aqueous acetone solution. These crystals are clear, light gray bulky plates. The crystal used was approximately 0·068 × 0·126 × 0·194 mm with [001] parallel to the φ axis of the goniometer. All X-ray studies were carried out using a General Electric XRD-5 diffractometer equipped with a single crystal orienter, with Cu Kα radiation, and at ambient room temperature (~21 °C).

Plots of the intensity weighted reciprocal lattice were used to determine the crystal symmetry. Cell constants were obtained from least-squares refinement using 27 independent 2θ measurements.

Crystal data

3,4:7,8-Dibenzotricyclo[4.2.0.0^{2,5}]octa-3,7-diene, C₁₆H₁₂. *a* = 10·716 (2), *b* = 7·706 (1), *c* = 6·719 (1) Å, β = 98·37 (2)°. Systematic absences: *h*0*l*, *l* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1. Space group: *P*2₁/*c* (No. 14). *Z* = 2; *F*(000) = 216; *V* = 548·86 Å³; μ = 5·38 (Cu Kα). λ(Cu Kα_{mean}) = 1·54178, Cu Kα₁ = 1·54050, Cu Kα₂ = 1·5433 Å.

Three-dimensional single-crystal intensity data were collected by the stationary-crystal stationary-counter method to the limit 2θ = 130° (Cu Kα₁), using a balanced nickel-cobalt filter pair. Of the 925 in-

dependent reflections measured the 717 whose net intensity exceeded 7 counts per second were considered to have observable intensity. The largest deviation from the average intensity for 6 periodically monitored reflections was 4%, indicating that the crystal had suffered neither serious radiation damage nor misalignment during the two days of data collection. The usual Lorentz and polarization factors were applied, as well as a correction for α_1 - α_2 splitting (Tulinsky, Worthington & Pignataro, 1959). The intensities were also corrected approximately for absorption (as a function of φ with the maximum correction factor being 1.22 (Silvers & Tulinsky, 1963). Standard deviations in the observed structure amplitudes, $\sigma(|F_o|)$, based on counting statistics, were calculated according to Evans (1961).

Determination and refinement of the structure

Phases for the structure solution were obtained by the symbolic addition procedure (Karle & Karle, 1966) after conversion of the data to normalized structure factor magnitudes $|E|$ by use of a K curve. The signs of 161 reflections (corresponding to 20 reflections/atom) were deduced in terms of one symbolic sign a , no phase indication being accepted at a probability lower than 0.999. Either sign for a seemed equally probable, so two E maps were computed. In the first E map there were 12 peaks ranging in magnitude of 724 to 1645 on an arbitrary scale. A reasonable chemical structure was not evident. The second map was then inspected and there were 8 peaks ranging in magnitude of 957 to 1507. A model of these peaks revealed the complete structure located at the inversion center at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

These 8 positions were refined isotropically by block-diagonal least-squares methods with unit weights to $R=0.142$ after five cycles. The refinement was continued with the temperature factors being converted to anisotropic temperature factors and retaining unit weights for five more cycles and $R=0.123$ was obtained.

A difference map was then calculated and only 6 peaks with an amplitude greater than $0.5 \text{ e.}\text{\AA}^{-3}$ were found. These peaks were in chemically reasonable positions to represent hydrogen atoms.

Before continuing the refinement, five reflections were remeasured, and one reflection, $\bar{1}11$, was omitted because of extinction. Five cycles of least-squares refinement, using statistical weights, varying overall scale factor, all positional parameters, hydrogen isotropic temperature factors and carbon anisotropic temperature factors served to complete the refinement at $R=0.069$. Final shifts in the positional parameters and non-hydrogen temperature factors were less than 0.1σ and the largest shift in any hydrogen temperature factor was 0.3σ with the other five less than 0.1σ .

The refinement was also carried out using the full-matrix least-squares calculation to $R=0.070$. A comparison of the two sets of positional parameters showed no significant differences, no carbon atom having

moved more than 0.006 \AA and no hydrogen atom having moved more than 0.06 \AA .

A final difference density map contained no features other than a randomly fluctuating background below $0.25 \text{ e.}\text{\AA}^{-3}$. Weights equal to $1/\sigma|F_o|^2$ were used in the least-squares calculations and the atomic scattering factors used were those of Stewart, Davidson & Simpson (1965) for hydrogen and of Cromer & Waber (1965) for carbon.

Calculations were carried out on a Control Data 6600 computer. Structure factor and least-squares calculations were done using a local modification of a program by Kartha (1964) and the Oak Ridge National Laboratory program ORNL-TM-305 (Busing, Martin & Levy, 1962). All Fourier computations were carried out using the Argonne National Laboratory program B-149 (Gvildys, 1965). Application of the symbolic addition method was facilitated by the use of the programs *SORTE66* (Bednowitz, 1966) and *EFACT* (Bednowitz, 1966). Various other data processing programs of local origin were used.

Final atomic parameters are given in Tables 1, 2 and 3. The estimated standard deviations were calculated from the inverse matrices of the final block-diagonal least-squares cycle; as usual, the true uncertainties are surely higher than these formally calculated standard deviations. The final R value for these parameters is 0.069 for the observed reflections only and 0.094 when all the data are included. Observed and calculated structure factor magnitudes from the final atomic parameters are shown in Table 4.

Table 1. Fractional atomic coordinates (not including hydrogen atoms)

The estimated standard deviation in parentheses refers to the last decimal position.

	x	y	z
C(1)	0.4521 (3)	0.6279 (5)	0.4920 (5)
C(2)	0.3184 (3)	0.5839 (5)	0.4042 (5)
C(3)	0.1950 (3)	0.6127 (6)	0.4283 (5)
C(4)	0.1044 (3)	0.5179 (6)	0.2972 (6)
C(5)	0.1405 (3)	0.4045 (6)	0.1567 (5)
C(6)	0.2653 (3)	0.3756 (6)	0.1359 (5)
C(7)	0.3531 (3)	0.4700 (5)	0.2652 (5)
C(8)	0.4938 (3)	0.4952 (5)	0.3324 (5)

Discussion of the structure

As illustrated in Fig. 1, DBTCO is in the *anti* configuration as required by the inversion center. These stereoscopic drawings (Johnson, 1965) show 50% equiprobability ellipsoids derived from the anisotropic thermal parameters. The least-squares plane for the eight carbon atoms in the asymmetric unit is given by the equation $0.0671x + 0.7432y - 0.6657z = 1.725$, with the largest deviation from the plane being 0.03 \AA ; the coefficients in the above equation are the direction cosines of the normal to the plane relative to \mathbf{a} , \mathbf{b} and \mathbf{c}^* . The central cyclobutane is also planar, as required

by the inversion center, and makes an angle of 111.1° with the least-squares plane described above.

Bond distances and angles involving only carbon atoms are given in Fig. 2, while those involving hydrogen atoms are shown in Fig. 3. The distances in the benzene ring average 1.383 Å. The two C(sp³)-C(sp²) bond distances, 1.507 and 1.523 Å, are not significantly different from one another or from the C(sp³)-C(sp²) bond in isobutene (1.505 Å; Bartell & Bonham, 1960).

In the central four-membered ring, the carbon-carbon distance (1.559 Å) for the formation of the

dimer is consistent with the slight elongation found in polysubstituted cyclobutanes, but the bridgehead bond (1.593 Å) is considerably longer than those found in other fused ring systems (Margulis, 1965; Einstein, Hosszu, Longworth, Rahn & Wei, 1967; Adman, Gordon & Jensen, 1968; Camerman, Weinblum & Nyburg, 1969; Camerman & Nyburg, 1969). It has been generally observed that in four-membered ring systems formed by the union of 5 or 6 membered rings, there is lengthening of the external bonds of the four-membered ring, rather than the bridgehead bonds. An

Table 2. Anisotropic thermal parameters

The temperature factor expression use was $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$. The estimated standard deviation in parentheses refers to the last decimal position.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.0070 (4)	0.0093 (7)	0.0170 (10)	0.0002 (5)	-0.0010 (5)	-0.0005 (8)
C(2)	0.0067 (4)	0.0113 (8)	0.0144 (9)	0.0004 (5)	-0.0005 (5)	0.0012 (7)
C(3)	0.0079 (4)	0.0160 (10)	0.0178 (10)	0.0019 (5)	0.0001 (5)	-0.0005 (9)
C(4)	0.0062 (4)	0.0216 (11)	0.0207 (11)	0.0006 (6)	-0.0003 (5)	0.0031 (10)
C(5)	0.0072 (4)	0.0158 (9)	0.0183 (10)	-0.0009 (5)	-0.0026 (5)	0.0008 (9)
C(6)	0.0082 (4)	0.0139 (9)	0.0156 (10)	0.0004 (5)	-0.0019 (5)	-0.0021 (8)
C(7)	0.0063 (4)	0.0114 (8)	0.0152 (10)	0.0007 (5)	-0.0003 (5)	0.0017 (8)
C(8)	0.0062 (4)	0.0124 (8)	0.0143 (9)	0.0004 (5)	0.0006 (4)	-0.0000 (8)

Table 3. Fractional coordinates and isotropic temperature factors for the hydrogen atoms

The estimated standard deviations in parentheses refer to the last decimal position.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
H(9)	0.473 (3)	0.745 (5)	0.492 (5)	4.9 (9)
H(10)	0.163 (3)	0.709 (5)	0.518 (5)	6.4 (11)
H(11)	0.010 (2)	0.542 (4)	0.320 (4)	2.2 (7)
H(12)	0.060 (3)	0.328 (4)	0.074 (4)	3.7 (9)
H(13)	0.292 (3)	0.287 (5)	0.047 (4)	3.6 (8)
H(14)	0.562 (2)	0.508 (4)	0.237 (4)	1.5 (6)

Table 4. Observed and calculated structure factor amplitudes

The columns headed F OBS and F CAL contain, respectively, |*0F*_o| and |*0F*_c|. Unobserved reflections are marked with * and observed reflections omitted from the final refinement are marked with X.

<i>h</i>	<i>k</i>	<i>l</i>	F OBS	F CAL	<i>h</i>	<i>k</i>	<i>l</i>	F OBS	F CAL	<i>h</i>	<i>k</i>	<i>l</i>	F OBS	F CAL	<i>h</i>	<i>k</i>	<i>l</i>	F OBS	F CAL
0	0	0	100	100	0	0	0	100	100										
0	0	1	80	80	0	0	1	80	80										
0	0	2	60	60	0	0	2	60	60										
0	0	3	40	40	0	0	3	40	40										
0	0	4	20	20	0	0	4	20	20										
0	0	5	10	10	0	0	5	10	10										
0	0	6	5	5	0	0	6	5	5										
0	0	7	3	3	0	0	7	3	3										
0	0	8	2	2	0	0	8	2	2										
0	0	9	1	1	0	0	9	1	1										
0	0	10	0	0	0	0	10	0	0										
0	1	0	70	70	0	1	0	70	70										
0	1	1	50	50	0	1	1	50	50										
0	1	2	30	30	0	1	2	30	30										
0	1	3	10	10	0	1	3	10	10										
0	1	4	5	5	0	1	4	5	5										
0	1	5	3	3	0	1	5	3	3										
0	1	6	2	2	0	1	6	2	2										
0	1	7	1	1	0	1	7	1	1										
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0	1	10	0	0	0	1	10	0	0										
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0	3	10	0	0	0	3	10	0	0										
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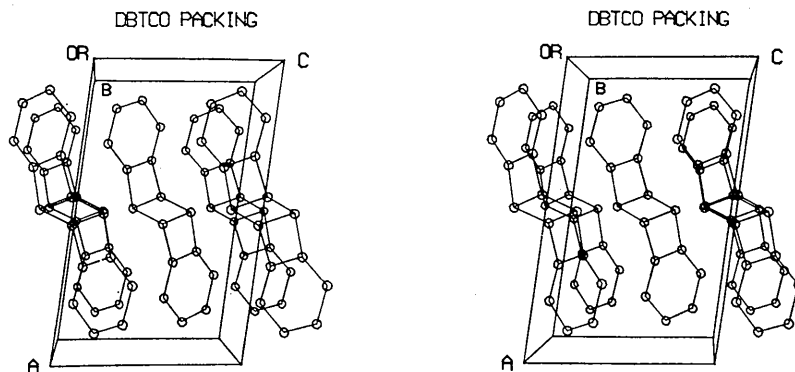


Fig. 4. Stereoscopic packing diagram. One unit cell is outlined.

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Refinement of the Crystal Structure of Sinigrin*

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The crystal structure of sinigrin (potassium myronate), $\text{KC}_{10}\text{H}_{16}\text{NO}_9\text{S}_2 \cdot \text{H}_2\text{O}$, has been refined on the basis of three-dimensional intensity data collected on an automated diffractometer. The final agreement index is 0.056 for 1906 reflections, and the estimated standard deviations in the atomic coordinates of the C, N, and O atoms are about 0.004 Å. The absolute configuration of the anion was confirmed from anomalous dispersion effects. The crystals are orthorhombic with space group $P2_12_12_1$. The unit-cell dimensions of a new crystal are $a = 8.265$ (1), $b = 11.440$ (3), and $c = 17.757$ (3) Å. An appreciable increase in the length of the c axis occurred during irradiation of the crystal. In addition, the vinyl group of the myronate ion appears to undergo large thermal motions. The distances between vinyl groups of adjacent myronate ions are such that a photopolymerization reaction between them would be possible, which might explain these two observations.

The X-ray crystallographic investigation of sinigrin, a salt of the formula $\text{K}^+(\text{C}_{10}\text{H}_{16}\text{O}_9\text{NS}_2)^- \cdot \text{H}_2\text{O}$ extracted

from the seeds of black mustard, was undertaken in the hope of supporting the organic-chemical work of M. Ettlinger and co-workers (Ettlinger & Lundeen, 1956, 1957; Ettlinger, Dateo, Harrison, Mabry & Thompson, 1961) on the structure of the anion, also

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