

probably has an appreciable contribution from internal torsional motion about the C(1)—NH₃⁺ bond (Trueblood & Dunitz, 1983); it is noteworthy that the principle eigenvector of **L**, when rigid-body motion is assumed, is only 12° from the direction of the C(1)—N bond. In attempting to assess this contribution, it is necessary to add additional atoms to avoid singularities, and for this purpose the three hydrogen-bonded Cl⁻ ions were included. The analysis was done using both the direct Dunitz—White approach, ignoring any correlation of internal and overall motion, and the approach of Schomaker & Trueblood (1984), including such correlations. In each case, the r.m.s. amplitude about the C—N bond was 5 (1)°; however, the analyses were flawed by the fact that one eigenvalue of **L** became slightly negative [mean square amplitude less than 1 (°)², smaller than its e.s.d.], presumably a consequence of the inclusion of the Cl⁻ ions in the analysis — they hardly can be expected to move in concert with the cation. Furthermore, the data are only of mediocre quality by the Hirshfeld (1976) test. Nonetheless, we believe this result is meaningful; it parallels the findings in many other structures containing this ion (Maverick, Grossenbacher & Trueblood, 1979; Trueblood & Maverick, 1979). At room temperature, the r.m.s. torsional amplitude about the C—N bond is about 12 (2)°.

The *tert*-butylammonium ion is hydrogen bonded to three neighboring Cl⁻ ions (Table 2), which are in nearly ideal positions for accepting these bonds, the N—H...Cl angles being nearly 180° and the C(1)—N...Cl angles about tetrahedral (104–109°). It is

characteristic of this ion in host–guest structures that it forms three hydrogen bonds in much this fashion, although often the receptor atoms in the guest structures are less ideally positioned (Cram & Trueblood, 1981; Maverick, Grossenbacher & Trueblood, 1979). There are no other short intermolecular (interionic) interactions.

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Dimethyl *exo*-5-(Dibromomethyl)-*endo*-5-methyl-6-oxobicyclo[2.2.2]octa-2,7-diene-2,3-dicarboxylate*

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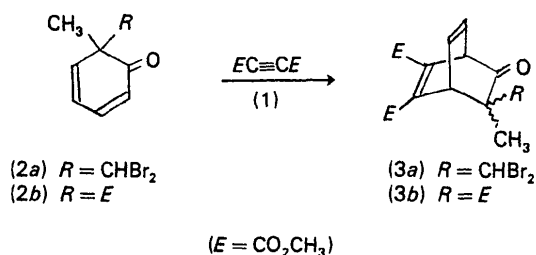
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Abstract. C₁₄H₁₄Br₂O₅, *M_r* = 422.1, monoclinic, *P*2₁, *a* = 7.859 (1), *b* = 10.406 (2), *c* = 9.888 (2) Å, β = 103.98 (1)°, *U* = 784.7 Å³, *D_x* = 1.79 Mg m⁻³, *Z* = 2, *Mo* Kα, λ = 0.71069 Å, μ = 5.13 mm⁻¹, *T* = 295 K, *F*(000) = 416, *R* = 0.032 for 1349 observed [*I* > 3σ(*I*)]

* Although the *endo* and *exo* designations are not strictly applicable to the bicyclo[2.2.2]octadiene system, we use them for the sake of simplicity with the following convention: substituents are designated as being *endo* or *exo* with respect to the unsaturated bridge of lower priority (Yates & Auksi, 1979).

reflections. Dimethyl acetylenedicarboxylate reacts preferentially on the methyl face of 6-(dibromomethyl)-6-methyl-2,4-cyclohexadien-1-one to give the title compound. In the bicyclo[2.2.2]octadiene system torsion angles (τ) about the double bonds are 0.4 (6) and 2.7 (7)°, while the C(5)—C(6) bond is slightly twisted [τ = 7.1 (5)°] due to contacts involving the CHBr₂ substituent. The two methoxycarbonyl groups are canted by 5.5 (8) and 78.1 (8)° with respect to the plane of the C(2)=C(3) double bond.

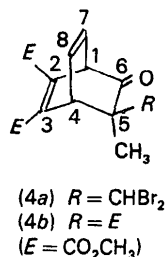
Introduction. In a continuation of our studies of the face selectivity of the Diels–Alder reaction of dimethyl acetylenedicarboxylate (1) with 6,6-disubstituted 2,4-cyclohexadiene-1-ones (Sawyer, Gomes & Yates, 1986), we have investigated the reaction of (1) with 6-(dibromomethyl)-6-methyl-2,4-cyclohexadien-1-one (2a) and found that it gives a mixture of epimers (3a) in an 8:1 ratio (Gomes, 1986). We report now on an X-ray crystallographic study of the structure of the major epimer formed on reaction of (1) with (2a). As we have pointed out previously, such results are of importance in both the synthetic utilization of this type of reaction and the elucidation of the factors affecting face selectivity in the Diels–Alder reaction.



Experimental. Reaction of (1) with (2a) (Wenkert, Wovkulich, Pellicciari & Ceccherelli, 1977) in a steel pressure bottle at 423–433 K for 4 h gave an 8:1 mixture of the epimeric adducts (3a), which were separated by chromatography on silica gel. Crystallization of the major isomer from diethyl ether gave clear, colorless crystals as well formed blocks, m.p. 425–426 K. A crystal described by the faces {100}, (01 $\bar{1}$), (0 $\bar{1}$ 1), (011), (0 $\bar{1}\bar{1}$), ($\bar{1}\bar{1}$ 1) and ($\bar{1}$ 11) which were 0.0113, 0.0132 ($\times 2$), 0.0162 ($\times 2$), 0.0125 and 0.0150 cm from an origin within the crystal was used throughout. Unit-cell dimensions by least-squares fit for diffracting positions of 25 reflections ($11.9 < \theta < 15.9^\circ$). Intensity data collected on an Enraf–Nonius CAD-4 diffractometer using ω – 2θ scans over ω scan ranges ($0.65 + 0.35 \tan \theta$)°. Scan rates conditional on information collected in prescans were selected to give an $I/\sigma(I)$ ratio of 25 within a max. scan time of 75 s. Backgrounds by extending scan by 25% on either side of peak were measured for half the time taken to collect the peak. Three standard reflections monitored every 6000 s of exposure time showed only statistical fluctuations. 2095 unique reflections in quadrant $h, k, +l$ with $2\theta < 55^\circ$ measured ($h: 0 \rightarrow 10, k: 0 \rightarrow 13, l: -12 \rightarrow 12$). Lorentz, polarization and absorption [program *ABSCOR* (*SDP* package); $8 \times 10 \times 8$ grid; min. T 0.290, max. T 0.379] corrections applied to all data. 95 systematic absences and reflections with $F_{\text{obs}} = 0.0$ rejected to give data set of 1928 reflections. Structure solution: Patterson function for two Br atoms, least-squares and Fourier calculations for other atoms; H atoms were located in ΔF Fourier maps or

were placed in calculated positions with $U = 8 \text{ \AA}^2$ but were not refined. All non-hydrogen atoms refined anisotropically. Refinement with alternative hand gave improved residuals. Least-squares refinement minimizing $\sum w\Delta F^2$ and including a correction for extinction [$g = 8 (1 \times 10^{-7})$] then converged (max. $\Delta/\sigma = 0.05$) to final agreement indices $R = 0.032$ ($wR = 0.035$) for 1349 observed data with $I > 3\sigma(I)$. Weights in final cycle given by $w = 4F^2[\sigma^2(I) + (0.03F^2)^2]^{-1}$. Most significant features in a final difference Fourier are some peaks $\leq 0.36 \text{ e \AA}^{-3}$ close to the Br atoms. Programs: Enraf–Nonius (1979) *SDP* package on PDP 11/23 computer. The final atomic positional and thermal parameters are included in Table 1; bond lengths and bond angles in Table 2.*

Discussion. The molecular structure (Fig. 1) establishes that the major epimer formed on reaction of dimethyl acetylenedicarboxylate (1) with 6-(dibromomethyl)-6-methyl-2,4-cyclohexadien-1-one (2a) is the *exo*-5-(dibromomethyl) isomer with the configuration shown in (4a).† The preferred attack of (1) is on the methyl face of (2a), as has been observed in the reaction of (1) with methyl 1-methyl-6-oxo-2,4-cyclohexadiene-1-carboxylate (2b), which gives a 3:1 mixture of epimers, (3b), of which the major one is the *exo*-5-(methoxycarbonyl) isomer (4b) (Sawyer, Gomes & Yates, 1986). It is noteworthy that this implies that steric effects are predominant in influencing the stereochemical course of the reaction of (1) with (2a), but not with (2b).



In the bicyclo[2.2.2]octadiene system, torsion angles about the double bonds C(2)–C(3) and C(7)–C(8) are 0.4 (6) and 2.7 (7)° respectively, while the large torsion angle C(1)–C(6)–C(5)–C(4) of 7.1 (5)° is presumably due to a Br(1)⋯O intramolecular contact of 3.196 Å (*ca* 0.15 Å less than van der Waals values). The C=C bond lengths [1.334 (8) and 1.313 (9) Å] are

* Lists of structure factor amplitudes, torsion angles and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43521 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† There is a difference in the formal numbering of (4a) and (4b), but for convenience of comparison we have numbered (4a) in analogy with (4b).

comparable to those observed in (4*b*) and related systems. Similarly the C(3)=C(2)—C(11) and C(2)=C(3)—C(13) angles have opened out to 123.6 (5) and 124.6 (5)° and the mean planes of the methoxy-

Table 1. Positional parameters (*e.s.d.*'s in parentheses) and isotropic or equivalent isotropic thermal parameters

	x	y	z	B(Å ²)
Br(1)	0.85100 (9)	1.000	0.62490 (6)	5.08 (1)
Br(2)	0.87143 (8)	0.76600 (9)	0.42658 (7)	4.62 (1)
O(1)	0.5348 (5)	1.1662 (4)	0.4441 (4)	4.7 (1)
O(2)	0.2295 (7)	1.1800 (6)	-0.0637 (5)	7.9 (1)
O(3)	0.1026 (6)	1.2102 (7)	0.1065 (5)	7.3 (1)
O(4)	0.6061 (6)	1.0431 (7)	-0.0593 (4)	8.0 (2)
O(5)	0.3681 (6)	0.9257 (5)	-0.1322 (4)	4.7 (1)
C(1)	0.3154 (6)	1.0386 (6)	0.2925 (5)	3.3 (1)
C(2)	0.3236 (6)	1.0592 (6)	0.1404 (5)	3.1 (1)
C(3)	0.4419 (6)	0.9852 (6)	0.1014 (5)	3.0 (1)
C(4)	0.5419 (7)	0.8962 (6)	0.2147 (5)	2.9 (1)
C(5)	0.6452 (6)	0.9842 (6)	0.3358 (5)	2.7 (1)
C(6)	0.5024 (7)	1.0743 (6)	0.3700 (5)	3.0 (1)
C(7)	0.2954 (7)	0.8957 (7)	0.3138 (6)	3.6 (1)
C(8)	0.4073 (7)	0.8214 (6)	0.2715 (5)	3.2 (1)
C(9)	0.7201 (7)	0.9027 (6)	0.4654 (6)	3.2 (1)
C(10)	0.7839 (7)	1.0651 (6)	0.2907 (6)	3.7 (1)
C(11)	0.2161 (8)	1.1547 (7)	0.0492 (6)	3.9 (1)
C(12)	-0.013 (1)	1.306 (1)	0.0241 (9)	9.2 (2)
C(13)	0.4830 (8)	0.9903 (7)	-0.0376 (5)	3.8 (1)
C(14)	0.389 (1)	0.9287 (9)	-0.2728 (6)	6.1 (2)
H(11)	0.2221	1.0769	0.3175	8*
H(41)	0.6186	0.8322	0.1799	8*
H(71)	0.2094	0.8533	0.3551	8*
H(81)	0.4000	0.7244	0.2769	8*
H(91)	0.6217	0.8578	0.4920	8*
H(101)	0.8750	1.0000	0.3066	8*
H(102)	0.7480	1.0832	0.1954	8*
H(103)	0.8131	1.1337	0.3468	8*
H(121)	-0.0820	1.3339	0.0839	8*
H(122)	-0.0820	1.3066	-0.0820	8*
H(123)	0.0813	1.3140	-0.0217	8*
H(141)	0.5000	0.8613	-0.2500	8*
H(142)	0.4160	1.0000	-0.3066	8*
H(143)	0.2834	0.9019	-0.3426	8*

Starred atoms were not refined. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{1}{3}[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table 2. Selected bond lengths (Å) and bond angles (°)

Br(1)—C(9)	1.946 (5)	C(1)—C(7)	1.515 (9)
Br(2)—C(9)	1.951 (5)	C(2)—C(3)	1.334 (8)
O(1)—C(6)	1.194 (6)	C(2)—C(11)	1.465 (8)
O(2)—C(11)	1.176 (7)	C(3)—C(4)	1.518 (7)
O(3)—C(11)	1.302 (7)	C(3)—C(13)	1.488 (7)
O(3)—C(12)	1.455 (9)	C(4)—C(5)	1.570 (7)
O(4)—C(13)	1.177 (7)	C(4)—C(8)	1.526 (7)
O(5)—C(13)	1.316 (7)	C(5)—C(6)	1.561 (7)
O(5)—C(14)	1.440 (7)	C(5)—C(9)	1.531 (7)
C(1)—C(2)	1.536 (7)	C(5)—C(10)	1.526 (7)
C(1)—C(6)	1.530 (7)	C(7)—C(8)	1.313 (9)
C(11)—O(3)—C(12)	117.4 (5)	C(6)—C(5)—C(9)	107.6 (4)
C(13)—O(5)—C(14)	117.1 (5)	C(6)—C(5)—C(10)	109.5 (5)
C(2)—C(1)—C(6)	101.2 (4)	C(9)—C(5)—C(10)	113.1 (4)
C(2)—C(1)—C(7)	107.7 (5)	O(1)—C(6)—C(1)	122.6 (5)
C(6)—C(1)—C(7)	106.7 (5)	O(1)—C(6)—C(5)	123.8 (5)
C(1)—C(2)—C(3)	113.5 (5)	C(1)—C(6)—C(5)	113.5 (5)
C(1)—C(2)—C(11)	122.9 (5)	C(1)—C(7)—C(8)	115.7 (5)
C(3)—C(2)—C(11)	123.6 (5)	C(4)—C(8)—C(7)	113.2 (5)
C(2)—C(3)—C(4)	114.3 (5)	Br(1)—C(9)—Br(2)	108.1 (2)
C(2)—C(3)—C(13)	124.6 (5)	Br(1)—C(9)—C(5)	114.3 (4)
C(4)—C(3)—C(13)	121.0 (5)	Br(2)—C(9)—C(5)	111.6 (4)
C(3)—C(4)—C(5)	106.7 (4)	O(2)—C(11)—O(3)	122.8 (6)
C(3)—C(4)—C(8)	107.6 (4)	O(2)—C(11)—C(2)	124.4 (6)
C(5)—C(4)—C(8)	107.1 (4)	O(3)—C(11)—C(2)	112.8 (5)
C(4)—C(5)—C(6)	104.5 (4)	O(4)—C(13)—O(5)	124.2 (5)
C(4)—C(5)—C(9)	109.8 (5)	O(4)—C(13)—C(3)	123.8 (5)
C(4)—C(5)—C(10)	112.0 (4)	O(5)—C(13)—C(3)	111.9 (5)

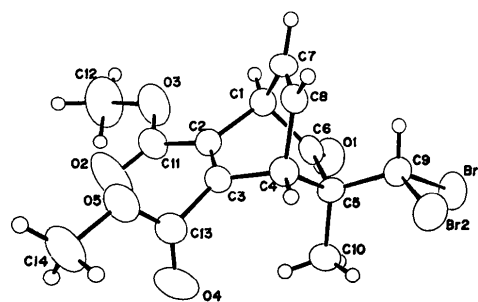


Fig. 1. ORTEP view (Johnson, 1965) of the molecule showing the numbering scheme used in the crystallographic refinements. Thermal ellipsoids are drawn at the 50% probability level. All H atoms are drawn with uniform isotropic thermal parameters.

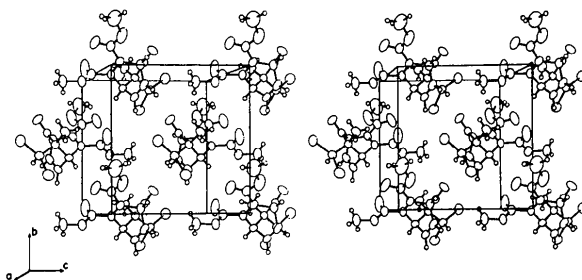


Fig. 2. Stereoscopic view down a of the crystal packing.

carbonyl groups are rotated by 5.5 and 78.1° [e.s.d. ca 0.8°] with respect to the plane through C(1)—C(2)=C(3)—C(4) from which C(11) and C(13) deviate by -0.039 (7) and -0.068 (6) Å, respectively. [Corresponding values for (4*b*) are: 122.6 (5), 128.2 (5), 12.4 and 79.7 (7)° and $\Delta C = -0.029$ (5), 0.066 (5) Å.]

The largest difference in bond angles between (4*a*) and (4*b*) is at C(5) where differences of ca 3° are observed. Intermolecular contacts are weak, the shortest being Br(2)···O(2)(1-x, $\frac{1}{2} + y$, -z) = 3.60 Å, Br(2)···H(71)(-1+x, y, z) = 3.05 Å and O(2)···H(41)(1-x, $-\frac{1}{2} + y$, -z) = 2.43 Å. A view of the crystal packing is given in Fig. 2.

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