action of the methylene groups in the former vibration would increase the potential energy of the vibration.

The band at 503 cm^{-1} [6–10,12,13] was assigned to C–C antisymmetric stretching, in which one of the bonds to the methylene carbon atom is stretched while the other is condensed. This assignment was made because the band was the strongest of those below 600 cm^{-1}; the bands at 875 and 666 cm^{-1}, which were also assigned to C–C stretching, were also stronger than the other bands assigned to skeletal vibrations.

Conclusions

The infrared and Raman spectra of 1,4,7-cyclononatriene can be completely explained on the basis of the C_{3v} *cis,cis,cis*-1,4,7-cyclononatriene crown structure. The similarity of the spectra of 2,5,8-cyclononatrienol and 1,4,7-cyclononatriene-d_2 to that of 1,4,7-cyclononatriene indicate that the former also possess a crown conformation.

Acknowledgments. We wish to acknowledge the generous assistance of Professor S. Winstein and his group, in particular Dr. H. Jones for providing pure samples of the compounds studied. The assistance of the staff of the Perkin-Elmer Corporation for providing the long-path cell, and Mr. Norman Mitchell of Applied Physics Corporation for taking the Raman spectra, and the generous financial support of the U. S. Atomic Energy Commission are greatly acknowledged.

The Crystal Structures of the Isomers *trans*- and *cis*-1,2-Dibromo-1,2-dicarbomethoxycyclobutane

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Abstract: *trans*-1,2-Dibromo-1,2-dicarbomethoxycyclobutane crystallizes in space group $P2_1/c$ with $Z = 4$ and cell parameters $a = 7.16$, $b = 13.18$, $c = 12.07$ A, and $\beta = 105° \, 11'$. *cis*-1,2-Dibromo-1,2-dicarbomethoxycyclobutane crystallizes in space group $P2_1/n$ with $Z = 4$ and cell parameters $a = 6.21$, $b = 11.21$, $c = 15.64$ A, and $\beta = 95° \, 55'$. The *trans* molecule possesses an approximate twofold axis while the *cis* molecule is completely asymmetric. In each isomer the cyclobutane ring is puckered with a dihedral angle near 150°.

In some cyclobutane derivatives, such as C_4Cl_8[1] and anemonin,[2] the four-membered ring is puckered whereas in other derivatives, such as 1,2,3,4-tetraphenylcyclobutane[3] and the dimer of cyclopentanone,[4] the four-membered ring is planar. The structure investigation of *trans*- and *cis*-1,2-dibromo-1,2-dicarbomethoxycyclobutane was undertaken in order to collect more information about the conformation of cyclobutane rings and to correlate the structural results with those from nuclear magnetic resonance studies on these molecules.[5]

Experimental Section

Crystals of both materials were prepared by Drs. E. Lustig and E. T. Ragelis of the Food and Drug Administration. They were in the form of colorless, elongated prisms. The *trans* and *cis* compounds had melting points of 86–87 and 40–40.5°, respectively. Each of the materials was somewhat volatile although it was possible to collect the diffraction data without the use of sealed capillaries. Cell dimensions were obtained from precession photographs, whereas intensity data were collected from multiple film, equi-inclination Weissenberg photographs with copper radiation and a nickel filter. The crystal of the *trans* compound was mounted parallel to the *c* axis while the crystal of the *cis* compound was mounted parallel to the *a* axis. The intensities were estimated visually by comparison with a calibrated film strip. They were corrected for Lorentz and polarization factors and spot size. The data were placed on an absolute scale by means of a K curve.[6] Space groups were determined unambiguously from the systematic absences. The cell parameters, space groups, and number of observed reflections are shown in Table I.

Table I. Experimental Data for the Isomers of 1,2-Dibromo-1,2-dicarbomethoxycyclobutane

	trans	*cis*
a, A	7.16 ± 0.02	6.21 ± 0.02
b, A	13.18 ± 0.02	11.21 ± 0.02
c, A	12.07 ± 0.02	15.64 ± 0.03
β	105° 11′ ± 15′	95° 55′ ± 15′
$\rho_{\text{X-ray}}$, g cm^{-3}	1.995	2.024
Space group	$P2_1/c$	$P2_1/n$
Total obsd refl	1714	1695
No. of refl obsd >0	1567	1430

Structure Analysis

The symbolic addition procedure for determining phases directly from the structure factor magnitudes[7] was used for both crystals. In each case the most probable set of signs proved to be the correct set. For equal atom problems, 10–12 reflections per atom in the asymmetric unit are sufficient to compute a well-resolved *E* map.[8] In the present investigations, with two Br atoms and twelve light atoms in each asymmetric

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(1) T. B. Owen and J. L. Hoard, *Acta Cryst.*, **4**, 172 (1951).

(2) I. L. Karle and J. Karle, *ibid.*, **20**, 555 (1966).

(3) J. D. Dunitz, *ibid.*, **2**, 1 (1949).

(4) T. N. Margulis, *ibid.*, **18**, 742 (1965).

(5) E. Lustig and E. P. Ragelis, *J. Am. Chem. Soc.*, in press.

(6) J. Karle and H. Hauptman, *Acta Cryst.*, **6**, 473 (1953).

(7) See *e.g.*, I. L. Karle and J. Karle *ibid.*, **16**, 969 (1963); **17**, 1356 (1964); **19**, 92 (1965).

(8) I. L. Karle, H. Hauptman, J. Karle, and A. B. Wing, *ibid.*, **11**, 257 (1958).

Table II. The Fractional Coordinates for *trans*-1,2-Dibromo-1,2-dicarbomethoxycyclobutane[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br (1)	0.9271	0.4770	0.3014	162	62	62	37	45	21
Br (2)	0.3599	0.2218	0.2902	111	57	55	22	19	−1
				B^b					
C(1)	0.1803	0.4109	0.3273	1.6					
C(2)	0.1537	0.2929	0.3315	2.0					
C(3)	0.1958	0.3042	0.4658	4.0					
C(4)	0.2852	0.4072	0.4548	3.2					
C(5)	0.2859	0.4570	0.2396	2.9					
C(6)	0.2817	0.4853	0.0467	5.1					
C(7)	0.9613	0.2464	0.2690	2.3					
C(8)	0.7271	0.2274	0.0905	5.0					
O(1)	0.4339	0.5001	0.2759	4.8					
O(2)	0.1932	0.4408	0.1383	3.0					
O(3)	0.8622	0.2009	0.3225	4.1					
O(4)	0.9220	0.2607	0.1595	2.8					
Standard error									
Br	0.0002	0.0001	0.0002	3	1	2	1	2	1
C	0.0025	0.0014	0.0016	0.4					
O	0.0018	0.0010	0.0011	0.4					

[a] For the Br atoms the thermal parameters are of the form $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Each β_{ij} is multiplied by 10^4. [b] Isotropic thermal parameter.

unit, 236 independent reflections with $|E| > 1.4$ produced E maps in which the Br atoms were clearly defined, but the light atoms were masked by diffraction ripples. It was necessary to include nearly all the observed data in order to obtain well-resolved maps. The final electron density maps for the *trans* and *cis* compounds are illustrated in Figures 1 and 2, respectively.

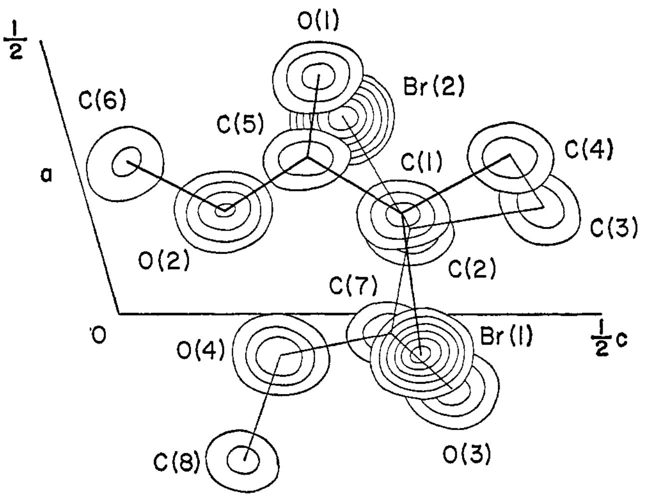

Figure 1. Sections from a three-dimensional electron density map of *trans*-1,2-dibromo-1,2-dicarbomethoxycyclobutane projected along the (010). The contours are spaced by 2 e A^{-3} beginning with the 2-e A^{-3} level, except for the Br atoms where every other contour is omitted.

The coordinates were subjected to a least-squares refinement in which the function $\Sigma(F_0 - F_c)^2$ was minimized. The atomic scattering factors were taken from the "International Tables for X-Ray Crystallography" (1962). During the isotropic refinement the scale factors for individual layers were varied. In the final cycles of refinement, the scale factors were kept constant and anisotropic temperature factors were used only for the Br atoms. The final R factors for the observed data were 11.1 and 9.6% for the *trans* and *cis* compounds, respectively.[9] The coordinates of the atoms in each crystal are listed in Tables II and III.

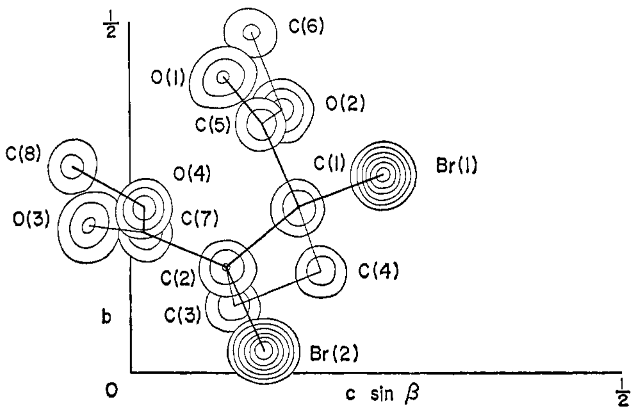

Figure 2. Sections from a three-dimensional electron density map of *cis*-1,2-dibromo-1,2-dicarbomethoxycyclobutane projected along the (100). The contours are spaced by 2 e A^{-3} beginning with the 2-e A^{-3} level, except for the Br atoms where every other contour is omitted.

Discussion

The geometry of the molecules is seen most easily by viewing the stereoscopic diagrams in Figures 3 and 4.[10] In each molecule the cyclobutane ring is bent. The dihedral angle between the planes which contain atoms C(1)–C(2)–C(3) and C(1)–C(4)–C(3) is 153° for the *trans* molecule and 150° for the *cis* molecule. In anemonin[2] the dihedral angle in the cyclobutane ring was found to be 152°.

The dihedral angles formed by the pair of planes containing Br(1)–C(1)–C(5) and C(2)–C(1)–C(4) and

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(9) Material supplementary to this article has been deposited as Document No. 8866 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $3.75 for photoprints, or $2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(10) Viewers can be obtained from Stereo-Magniscope, Inc., Elmhurst 73, N. Y., for 35¢.

Table III. The Fractional Coordinates for *cis*-1,2-Dibromo-1,2-dicarbomethoxycyclobutane[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br (1)	0.4610	0.2786	0.2606	180	66	20	−2	13	−10
Br (2)	0.5059	0.0299	0.1354	181	50	26	22	25	2
				B[b]					
C (1)	0.2353	0.2328	0.1737	1.6					
C (2)	0.2892	0.1462	0.0989	1.8					
C (3)	0.0545	0.0933	0.1047	1.9					
C (4)	0.0595	0.1427	0.1958	2.1					
C (5)	0.1424	0.3525	0.1375	2.2					
C (6)	0.8390	0.4805	0.1224	3.7					
C (7)	0.3391	0.2013	0.0159	2.3					
C (8)	0.6032	0.2949	0.9370	3.2					
O (1)	0.2402	0.4197	0.0948	4.5					
O (2)	0.9454	0.3716	0.1550	3.0					
O (3)	0.2081	0.2082	0.9540	4.4					
O (4)	0.5407	0.2333	0.0165	2.6					
Standard error									
Br	0.0004	0.0001	0.0001	9	1	1	2	2	1
C	0.0033	0.0012	0.009	0.3					
O	0.0026	0.0010	0.0007	0.3					

[a] The thermal parameters for the Br atoms are of the form $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Each β_{ij} is multiplied by 10^4. [b] Isotropic thermal parameter.

by the pair Br(2)–C(2)–C(7) and C(1)–C(2)–C(3) are near 89° in both isomers. The atoms in the four -CCOO- groups (two in each isomer) are nearly coplanar. The largest deviation of any atom from the least-squares planes is 0.008 A except for C(7) in the *cis* molecule which deviates by 0.02 A. The -CCOO- planes, however, are twisted away from the Br(1)–C(1)–C(5) and Br(2)–(C2)–(C7) planes by angles of 61 and 67° in the *trans* molecule and 68 and 41° in the *cis* molecule. In this twisted configuration the intramolecular Br···O distances are at least 3.0 A.

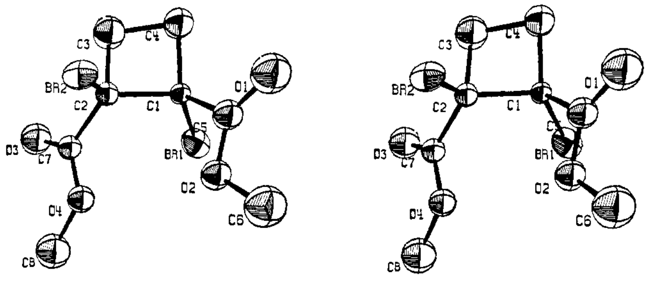

Figure 3. Stereoscopic diagram for *trans*-1,2-dibromo-1,2-dicarbomethoxycyclobutane.

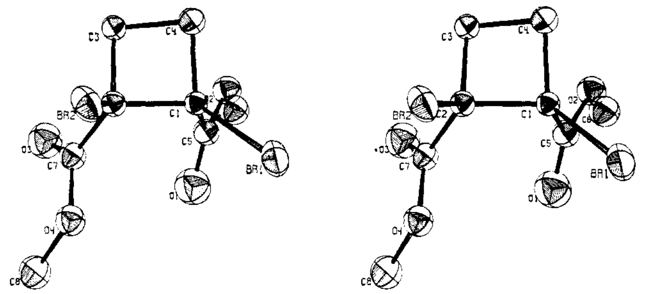

Figure 4. Stereoscopic diagram for *cis*-1,2-dibromo-1,2-dicarbomethoxycyclobutane. The drawing was made by a computer program prepared by C. K. Johnson, OR TEP, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

The *cis* molecule is completely asymmetric, whereas the *trans* molecule has an approximate twofold axis which passes through the halfway points between atoms C(1), C(2) and C(3), C(4). The configuration for the *trans* molecule is very similar to that found in anemonin[2] in which two lactone groups are in the *trans* position with respect to the cyclobutane ring. Lustig and Ragelis[5] have found that in solution, however, the configuration of the *cis* molecule as determined from nmr spectra is somewhat different. The 60- and 100-mHz proton spectra show only one peak for the CH_3 protons, and AA′BB′ patterns for the ring protons. Thus, on the nmr time scale, both molecules when in solution possess twofold symmetry; that is, on the average, the *cis* molecule has a planar ring (C_s) and the *trans* molecule has a planar or twisted ring (C_2). A complete report on the nmr spectra will be given in a forthcoming publication.[5]

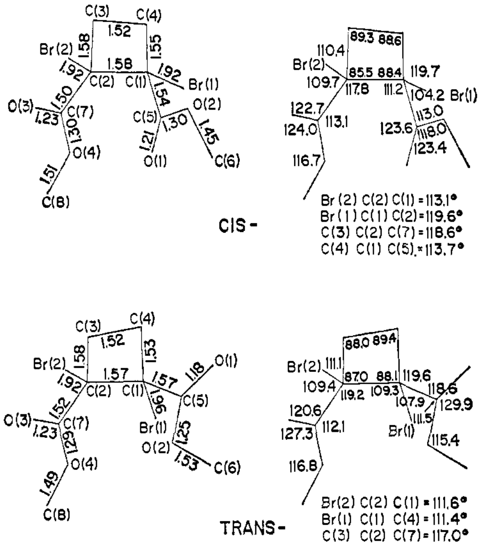

Figure 5. Bond distances and angles. The standard deviations are of the order of 0.019 A for C–Br bonds, 0.027 A for all other bonds, and 1.1° for the angles.

As viewed in Figures 3, 4, and 5, the left-hand sides of both isomers are very similar. In the *trans* isomer,

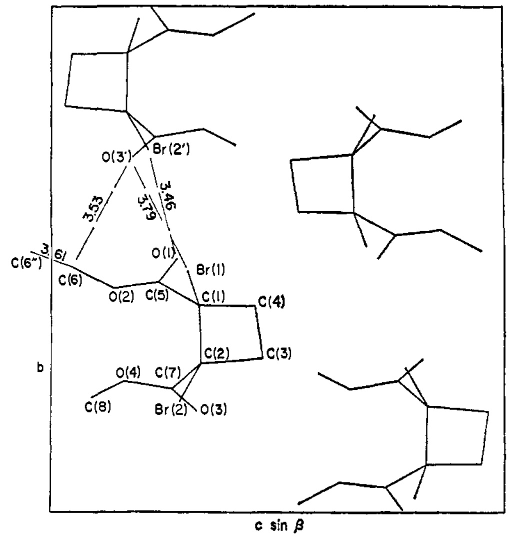

Figure 6. Contents of a unit cell and nearest intermolecular approaches for the *trans* molecule. Two other intermolecular distances less than 3.8 A are 3.73 A between O(1) and Br(1''') of the molecule at 1 + *x* and 3.69 A between Br(2) and O(3''') of the molecule at 1 + *x*.

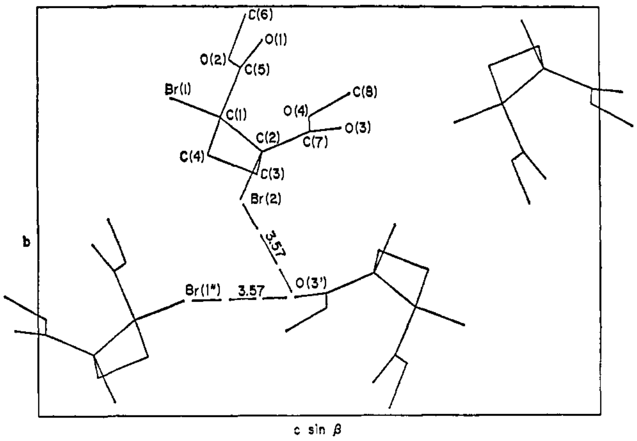

Figure 7. Contents of a unit cell and nearest intermolecular approaches for the *cis* molecule. Three other intermolecular distances less than 3.8 A occur between one molecule and another translated by 1 + *x*. They are O(1)–C(6''') at 3.76 A, Br(2)–C(3''') at 3.56 A, and Br(2)–C(4''') at 3.69 A.

both Br atoms are closer to the ester O atoms rather than to the carbonyl O atoms. On the other hand, in the *cis* isomer, while Br(2) is closer to the ester O(4) than to the carbonyl O(3), the -CCOO- group adjacent to Br(1) is twisted in an opposite direction so that Br(1) is closer to the carbonyl O(1) rather than the ester O(2).

Bond distances and angles for the two compounds are illustrated in Figure 5. In the presence of the two Br atoms for each molecule, the coordinates for the lighter atoms are not too well determined, especially with visually estimated data. Hence there is little point in discussing individual bond lengths. Mention should be made that in some cyclobutane derivatives such as C_4F_8,[11] C_4Cl_8,[1] 1,2,3,4-tetraphenylcyclobutane,[3] and the photodimer of cyclopentanone,[4] the C–C bond lengths in the cyclobutane ring ranged from 1.54 to 1.60 A. In this investigation the C–C lengths in the two cyclobutane rings ranged from 1.52 to 1.58 A, but with a standard deviation of 0.027 A these values are not particularly meaningful.

An interesting feature involving the CCBr angles was observed. All the CCBr angles in the *trans* isomer and the three CCBr(2) angles in the *cis* isomer range from 107.9 to 113.7°; however, the angles C(2)–C(1)–Br(1) and C(4)–C(1)–Br(1) in the *cis* isomer have values of 119.6 and 119.7°, respectively. The increase in these angles gives rise to an increase in the Br···Br separation in the *cis* molecule. The value of this separation is 3.4 A.

The contents of the unit cell of each isomer is shown in Figures 6 and 7. There are no intermolecular distances smaller than 3.5 A. The shortest approaches between atoms of different molecules occur mostly between Br and O atoms.

Acknowledgment. We are indebted to Mr. S. Brenner for preparing the computer programs and to Dr. D. Mitchell for executing the computations.

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[11] H. P. Lemaire and R. L. Livingston, *J. Am. Chem. Soc.*, 74, 5732 (1952).