

78-7; 11, 34731-79-8; 12, 34731-80-1; 13, 34731-81-2; 15, 32811-83-9; dimethyl 1-methoxy-cis-cyclopropane-1,2-dicarboxylate, 30630-35-4; dimethyl 1-*tert*-butoxy-cis-cyclopropane-1,2-dicarboxylate, 30630-40-1.

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Conformational Analysis. LXXXV. The cis,cis-1,6-Cyclodecadiene System^{1,2a}

N. L. ALLINGER,^{*2b} M. T. TRIBBLE,^{2c} AND J. T. SPRAGUE^{2d}

Departments of Chemistry, Wayne State University, Detroit, Michigan 48202,
and University of Georgia, Athens, Georgia 30601

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Molecular force field calculations were carried out on cis,cis-1,6-cyclodecadiene and on cis,cis-cyclodeca-3,8-diene-1,6-dione. The former is calculated to be a 65:35 mixture of chair and boat forms. The bond lengths and angles are in good agreement with the electron diffraction values. The dione is calculated to be a mixture of chair, boat, half-boat in the ratio of 0.59, 0.32, 0.09. Bond lengths and angles are predicted. The dipole moment of the mixture is calculated to be 1.5 D and measured experimentally as 1.4 D. The heats of formation were also calculated.

A great many studies have been reported on the conformational analysis of the 1,6-cyclodecadiene ring system (I) during the past several years.³⁻¹⁴ These have included a variety of nmr studies of the hydrocarbon itself and a number of derivatives, an electron diffraction study of the hydrocarbon (I) in the gas phase, and an X-ray study of the crystalline dione derivative (II), among others. In each case it was

concluded that the chair conformation (Ia, IIa) was the predominant or exclusive structure present.

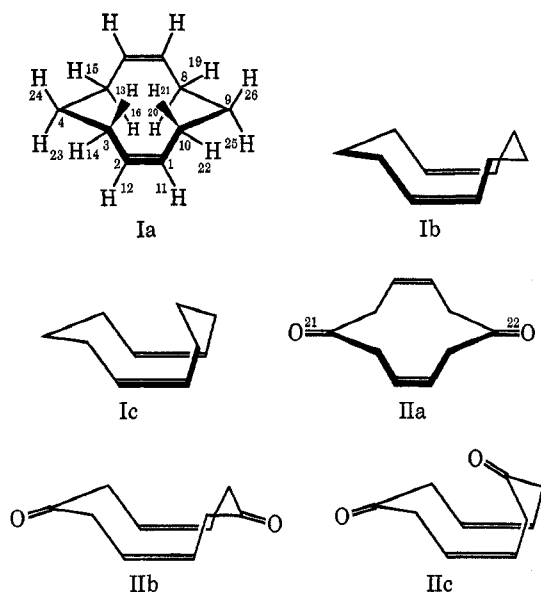
Earlier papers have described force field calculations which permit us to determine with reasonable accuracy the molecular geometries and conformational energies of various kinds of molecules, including alkanes,¹⁵ alkenes,¹ and ketones.¹⁶ The calculations deal with all of the usual steric effects, torsion, etc., and a classical electrostatic calculation between dipoles is used to allow for interaction between polar groups (double bonds and carbonyl groups).¹⁷

We have studied the three conformations which models indicate most probable: The chair conformation of symmetry C_{2v} (a), the boat conformation of C_{2v} (b), and a conformation of symmetry C_s (c). We have examined separately the parent hydrocarbons I, and also the diketo derivatives II.

Our calculations give relative energies for Ia, Ib, and Ic of 0.0, 0.34, and 5.01 kcal/mol, respectively. These calculations suggest that the chair conformation (Ia) will predominate over the boat (Ib) by about 65:35 at room temperature, and the amount of the C_s conformation will be negligible. Since the two former structures each have a symmetry number of 2, the predominance of the chair form will increase with a lowering of temperature, and this seems to be consistent with the electron diffraction work. The available experimental nmr work has been interpreted in terms of a single stable conformation (Ia) at low temperatures, which rapidly inverts at higher (room) temperature.

The calculated structure for the chair form is compared with the electron diffraction structure in Table I.

Dale^{5,6} has suggested from double bond isomerization studies in some C_6 - C_{24} cyclic dienes that in the C_8 , C_{10} , and C_{14} ring series the conformation with the cis double bonds diametrically opposed is a "strain-free" one, due to the lack of intramolecular van der Waals contact between ring hydrogens and the double bond



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TABLE I
CALCULATED AND EXPERIMENTAL STRUCTURES OF
Ia AND IIa (CHAIR FORMS)

	— <i>cis,cis</i> -1,6-Cyclodecadiene—		<i>cis,cis</i> -Cyclodeca- 3,8-diene-1,6-dione, calcd
	Calcd	Obsd ^a	
C ₁ =C ₂	1.342	1.326 ± 0.006 Å	1.341
C ₂ -C ₃	1.508	1.506 ± 0.006 Å	1.505
C ₃ -C ₄	1.535	1.534 ± 0.006 Å	1.515
C ₁ -H ₁₁	1.096	1.102 ± 0.012 Å	1.096
C ₄ -H ₂₃	1.101	1.112 ± 0.004 Å	1.223 (C ₄ =O ₂₃)
C ₁ C ₂ C ₃	128.7	128.2 ± 0.3°	128.0
C ₂ C ₃ C ₄	112.4	112.8 ± 0.3°	111.4
C ₃ C ₄ C ₅	112.9	114.1 ± 0.6°	117.6
C ₁ C ₂ H ₁₂	118.0	116.6 ± 1.0°	118.2
H ₂₃ C ₄ H ₂₄	105.5	105.6 ± 1.0°	121.2 (C ₃ C ₄ O ₂₃)
Heat of forma- tion gas phase, 25°, kcal/mol	+8.88		-42.02
^a Reference 12.			

π cloud. Our calculations indicate that Ia possesses a strain energy of 6.01 kcal/mol, much of which involves the two *cis* double bonds. The repulsion between carbons 1 and 7 in Ib amounts to 0.3 kcal/mol. This repulsion is therefore small, but not negligible.

The ketone derivatives II were also studied. As far as their relative energies, IIa and IIb do not differ much from the hydrocarbons. The chair form is again the more stable, by 0.35 kcal/mol. Approximately 0.1 kcal/mol of this energy difference is due to each of the following: torsion, van der Waals, dipole-dipole. In this case, the *C_s* conformation is calculated to be only 1.56 kcal/mol higher in energy than the chair conformation. It is in addition favored by entropy, since its symmetry number is only 1. Thus we calculate that IIa, IIb, and IIc will constitute mole fractions of 0.59, 0.32, and 0.09 in the molecular mixture in benzene solution (dielectric constant equals 2) at room temperature.

The relatively higher stability of the *C_s* conformation with the diketone, as opposed to the hydrocarbon, results from the absence of the hydrogen on the methylene group which is pointed back over the molecule. The dipole-dipole interaction energy in this conformation is actually favorable, by 0.2 kcal/mol, compared to the chair. The favorable energy can be ascribed to an attraction between the oxygen on the right in IIc and the carbonyl carbon on the left.

X-Ray crystallography has indicated that the dione exists as the chair form (IIa) in the crystal. The bond angles and bond lengths have not yet been reported. Our calculated bond angles and bond lengths are given in Table I.

To show that the molecule existed as a mixture of conformations in solution, we studied the dipole moment experimentally. The dipole moments calculated for IIa, IIb, and IIc are respectively 0, 1.63, and 3.67 D. However, because of vibrational motion (atomic polarization) we anticipate that IIa will actually show a dipole moment of about 0.7 D (as is shown by the analogous *p*-benzoquinone,¹⁸ for the same reason). From our calculated mole fractions and these moments for the individual conformations, the calculated dipole moment¹⁹ for the mixture is 1.53 D. If the 0.7 D moment for conformation IIa was instead taken to be 0, the calculated apparent moment for the mixture was 1.43 D. The observed moment, in benzene solution, was 1.40 ± 0.02 D. The calculated and experimental values are thus in good agreement. It may be noted that the size of the observed moment depends quite strongly on the 9% of the *C_s* conformation. If this conformation were not present, then conformations IIa and IIb would be present in mole fractions of 0.64 and 0.36, respectively. This mixture would give a calculated dipole moment of 0.98–1.13 D, depending on whether the 0.7 D moment for conformation IIa was or was not used.

Thus we conclude that for both the hydrocarbon and diketone, the major conformation in solution is, as previously suggested by others, the chair. The other conformations are, however, present in substantial amounts, and significantly affect the properties of the compound.

Experimental Section

A sample of *cis,cis*-cyclodeca-3,8-diene-1,6-dione (II) was kindly provided by Dr. J. J. Vollmer,²⁰ and was used as obtained.

The dipole moment measurements were carried out on benzene solutions at 25° using previously described procedures, apparatus, and calculations.²¹

Registry No.—Ia, 1124-79-4; IIa, 20771-23-7.

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