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THE EXISTENCE OF THE FLEXIBLE CONFORMATION IN SIX-MEMBERED RINGS

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ABSTRACT

From consideration of electrical polarization and nuclear magnetic resonance measurements, 1,4-dimethylenecyclohexane and its exo-tetramethyl and tetraphenyl analogues have been assigned the flexible ring conformation, as have also 1,4-dithiane and *cis*-1,4-dithiane-1,4-dioxide. However, the magnitudes of the moments indicate that uniform flexibility is not prevalent, the stretched form being predominant. In contrast to these flexible forms the conformation of dithiane monoxide is thought to be chair and that of 2,5-diphenyl-1,4-dithiin a fixed boat.

Evidence is accumulating to show that the Sachse-Mohr chair conformation for sixmembered rings is not universal (1), and in some instances is less likely than the so-called "flexible" form of conformation (2). It has been shown by Kumler and Huitric (3) that the electric dipole moments of α -halogenocyclohexanones are best explained by some contributions from flexible forms. Correlation of dipole moments with nuclear magnetic resonance spectra of N,N'-disubstituted piperazine seems to show that these substances are entirely in the flexible form. Indeed the moment of 1,4-cyclohexanedione ($\mu = 1.3$ D) (4), which has been interpreted in terms of an equilibrium mixture of cis and trans forms (boat and chair in the conformational sense), might better be included among substances in which a dynamic structure (flexible form) is operative. At least this is our interpretation of the fact that only one peak is found in the n.m.r. spectrum of this substance, whereas rigid-boat and chair conformations both ought to display distinctive axial and equatorial hydrogen resonance if they persist longer than 0.01–0.02 second.

The carbonyl groups in the cyclohexanones and cyclohexanedione would contribute 120° angularity to the six-membered rings of which they are a part in consequence of their sp^2 bond distribution.



It seems to be worthwhile to examine analogues with this structural feature so we have synthesized 1,4-dimethylenecyclohexane (I, R = H), its exo-tetramethyl homologue (I, $R = CH_3$), and have included the already known 1,4-bis-diphenylmethylidenecyclohexane (5) (I, $R = C_6H_5$). Structure I depicts these molecules in the non-boat (the stretched) mode of the flexible six-membered ring.

The preparation of 1,4-dimethylenecyclohexane, II, by pyrolysis of the 1,4-diacetoxymethylcyclohexane, II, has been effected according to Bailey's method (6) for synthesis of the 1,2-structural isomer. Bailey's recommended use of the primary rather than the tertiary dialcohol minimizes the isomers which are ring unsaturated but it cannot prevent dehydrogenation and hydrogen redistribution. Notwithstanding a low yield of acetic acid

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(61%) at a pyrolysis temperature of 500°, this temperature has been chosen in order to minimize the formation of xylene and other aromatic hydrocarbons.

Although the complexity of the crude product precludes separation of the ringunsaturated isomers of 1,4-dimethylenecyclohexane (I, R = H), the presence of the conjugated isomers is readily discernible because I is transparent throughout the ultraviolet range to 215 m μ . Moreover the conjugated diene impurities can be removed by use of diethyl azodicarboxylate, with which they form Diels-Alder complexes. The fortuitous boiling point (122°) of I makes separation from toluene and xylene by fractional distillation a relatively simple operation. If 1,4-dimethyl-2,5- or -1,4-hexadienes were present in the system they have escaped detection by us.

Except for a tendency toward slow polymerization, which might be expected in view of similarity with isobutylene, the purified substance is stable under neutral conditions, especially in absence of oxygen. Upon ozonization only formaldehyde and 1,4-cyclo-hexanedione can be isolated. On the other hand extensive isomerization occurs upon treatment with acid; among the isomer products the thermodynamically more stable 1,4-dimethyl-1,3-hexadiene has been identified by its ozonization product, acetonyl-acetone.

The infrared spectrum of 1,4-dimethylenecyclohexane contains all the expected absorptions of the exo unsaturation. The CH_2 -hydrogen out-of-plane deformation is indicated strongly by the absorption at 893 cm⁻¹ and, weakly, by what is probably its overtone at 1780 cm⁻¹. The C—H stretching of the double bonds is indicated at about 3080 cm⁻¹; the in-plane deformation is displaced to 1405 cm⁻¹ from its expected position at 1420-1410 cm⁻¹, and the C—C stretch is strong at 1660 cm⁻¹.

It is of interest that this exocyclic unsaturation behaves typically toward iodine according to the spectral behavior reported by Long and Neuzil (7) for unsymmetrically disubstituted alkenes since only a single peak at 293 m μ is observed when 1,4-dimethylene-cyclohexane is treated with iodine. Thus it would seem that the double bonds in 1,4-dimethylenecyclohexane are of themselves quite normal.

The exo unsaturation of 1,4-dimethylenecyclohexane can be preserved during bromine addition and elimination under conditions (exclusion of peroxides by diphenylamine) where the radical reaction is at least not excluded. Only one tetrabromide has been found in the product, indicating to us that an equilibrium mixture of chair and boat conformations is less likely than either a chair or a flexible conformation alone.

On the other hand methoxymercuration leads to two geometric isomers, approximately in equal amount. In view of the stereospecificity of this addition with simple alkenes the formation of two isomers, especially where one is not preponderant, is less to be expected from a chair conformation than from the flexible form since the median shape of this latter is essentially colinear with respect to alkene groups. It is of interest that the reversal of oxymercuration when it is accomplished with concentrated hydrochloric acid regenerates pure 1,4-dimethylenecyclohexane, thus indicating that the process is molecular rather than ionic.

In respect of nuclear magnetic resonance 1,4-dimethylenecyclohexane behaves like 1,4-cyclohexanedione in favor of a flexible conformation. Only two peaks are observed from an undiluted sample at 25°. The peak at 20 c.p.s. must represent the methylidene hydrogens because the area enclosed by it is half of that to be attributed to the ring methylene hydrogens which occurs at 107 c.p.s. in a 60 Mc field. We have been unsuccessful in the attempts to split this absorption into axial and equatorial hydrogen resonance by lowering the temperature of a solution in carbon disulphide to -120° .

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A similar study has been made with 1,4-diisopropylidenecyclohexane (I, R = CH₃) which we have prepared via the *cis*-1,4-glycol from methyl chloride Grignard reagent and diethyl 1,4-cyclohexanedicarboxylate (mainly cis). Mild acid treatment converts the cis glycol to trans with loss, whereas stronger treatment dehydrates it cleanly to the exo dialkene. This structure has been demonstrated by ozonization to acetone and 1,4-cyclohexanedione. Like its lower homologue it is ultraviolet-transparent down to 210 m μ and only one tetrabromide is obtained from it.

It is to be expected that this substance would show only two absorptions by n.m.r., and in fact in carbon disulphide one peak at 130 c.p.s. with area corresponding to the methyl hydrogens and the other peak of larger area at 97 c.p.s. have been observed. The hope that the latter peak would split when the temperature was lowered has not been realized because no suitable solvent has been found for the examination at low temperatures.

Equally unsuccessful has been the attempt to discover axial and equatorial absorption for 1,4-bis-diphenylmethylidenecyclohexane. This substance is so insoluble in appropriate organic solvents that its n.m.r. spectrum (40 Mc) can only be obtained in tetrachloroethane at 130°. The spectrum at this temperature consists of one peak at -53 c.p.s. characteristic of phenyl hydrogens and the other at +137 c.p.s. characteristic of the ring methylene hydrogens, both relative to the solvent. At room temperature tetrachloroethane has a peak 239 c.p.s. (at 40 Mc) below tetramethylsilane.

Because strongly polar groups are absent in these exo-unsaturated cyclohexanes the electrical polarizations are relatively meaningless but they have been studied. Firstly, the distortion polarizations have been determined when possible. Since 1,4-dimethylene-cyclohexane is a liquid at room temperature the electric polarization $(P_{\rm E})$ at optical frequencies has been used; likewise with dimethyl sulphoxide to be discussed later. The distortion polarizations $(P_{\rm D} = P_{\rm E} + P_{\rm A})$ of the remainder (the solids) have been determined by the wafer technique (8, 9) and are listed among others in Table I together with

Distor	tion polarizat	ion measurer	nents			
				Me	ol. refract	ion
Substance	d_{4}^{20}	e	$P_{\mathbf{E}+\mathbf{A}}$	Eisen- lohr	$\begin{array}{c} \text{Vogel} \\ \text{C}_{\text{ali}} \end{array}$	Vogel Car
1,4-Dimethylenecyclohexane Bis-isopropylidenecyclohexane Bis-diphenylmethylidenecyclohexane 2,5-Diphenyl-1,4-dithiin 1,4-Dithiane 1,4-Dithiane monoxide <i>trans</i> -1,4-Dithiane-1,4-dioxide <i>cis</i> -1,4-Dithiane-1,4-dioxide	$\begin{array}{c} 0.821 \\ 1.025 \\ 1.159 \\ 1.363 \\ 1.376 \\ 1.433 \\ 1.516 \\ 1.537 \end{array}$	$\begin{array}{c}1.4717^{*}\\2.70\\2.64\\3.038\\2.682\\2.825\\2.992\\3.094\end{array}$	$\begin{array}{r} 36.9^*\\ 58.0\\ 126\\ 79.5\\ 31.4\\ 35.9\\ 40.0\\ 40.6\end{array}$	$36.0 \\ 54.5 \\ 132 \\ 70.0 \\ 31.0$	$\begin{array}{r} 36.2 \\ 54.8 \\ 134 \\ 72.4 \\ 34.4 \\ 34.3 \\ 34.1 \\ 34.1 \\ 34.1 \end{array}$	71.6

TABLE⁻ Istortion polarization measurements

*Actually $n_{\rm D^{20}}$ and $P_{\rm E}$ for this liquid.

values calculated by the summation of atom (Eisenlohr) or bond (Vogel) polarizabilities. Only three items in the table warrant comment. It may be seen that additive MR_D for bis-1,4-diphenylmethylidenecyclohexane is appreciably higher than the P_D values obtained from the dielectric constant of wafers and absurdly so, as will be shown by comparison with total polarization of bis-diphenylmethylidenecyclohexane solutions. This discrepancy conforms with earlier studies (10) and it leads us to prefer the wafer

technique for evaluation of $P_{\rm D}$. This preference applies to a second item, $P_{\rm D}$ for dithiane. In this instance the agreement with additive polarizability by the Eisenlohr calculation is good, although inconsistent with the Vogel bond additivity.

The third item for comment in Table I is 2,5-diphenyldithiin, because the distortion polarization determined by dielectric constant is 8.1 cc higher than the average of the summation values for MR_D despite the presence of the phenyl groups which would be expected to cause P_D to be lower than MR_D by summation of atom or bond polarizabilities. One must presume in this instance that an appreciable exhaltation in electronic polarization (P_E) is operative, a situation not unexpected in view of the divinyl sulphide linkage in this substance.

The dipole moments and data from which they are derived are shown for the substances of this report in Table II. As would be expected from resemblance to isobutylene and tetramethylethylene the moments of dimethylenecyclohexane and diisopropylidenecyclohexane are indistinguishable from zero at our present precision. However, a small moment may be attributed to bis-diphenylmethylidenecyclohexane on the basis of the measured distortion polarization. The use of MR_D by summation would lead to an absurd result. But the assignment of flexible conformation to these exo-unsaturated cyclohexanes depends not upon the moment but upon the absence of axial-equatorial peaks in the n.m.r. spectra.

In earlier publications from this laboratory the flexibility of several six-membered ring systems has been attributed entirely on geometrical grounds to the 120° ring angles contributed by carbonyl or nitramino (11) linkages as a consequence of their sp_2 hybridization. To be sure, the same type of flexible conformation is required for explanation of the appreciable moments of 1,4-diphenyl- (12) and 1,4-dimethyl-piperazines (8) in which tertiary amino groups are involved in the ring. But the 110–111° R—N—R angle of amines is an extreme form of the group which is oscillating with inversion. The flexibility of the diphenyl- or dimethyl-piperazine may then be attributed to the 120° ring angles which amino nitrogen must contribute in the planar median of the oscillation if it is assumed that the nitrogen atom oscillation rate of the flexible ring must be 10^3-10^4 c.p.s. and that of the substituted amino group will be less than 10^7 c.p.s. the assumption of an effective 120° angles is not unreasonable, especially since one frequency might be expected to "lock in" to the other.

The question arises whether the flexible conformation is likely in absence of sp_2 angularity. An answer may be provided by consideration of 1,4-dithiacyclohexanes since information about bond lengths and bond angles of 1,4-dithiane (13) and *trans*-1,4-dithiane-1,4-dioxide (14) is available. Although these data are based on diffraction studies which specify chair conformations in the crystalline state it may be assumed that they will be applicable if the substances exist in solution as flexible forms.

The dipole moments of the 1,4-dithiacyclohexanes and their oxides are listed in Table II. The apparent moment of 1,4-dithiane ($\mu = 0.51-0.56$ D) is small but the precision of the determination of $P_{\rm D}$ (Fig. 1) and of total polarization ($P_{\rm T}$, Fig. 2) in benzene solution from 20 to 40° C indicates that this moment is real and is temperature dependent. The existence of the meagre moment is not surprising in view of the comparable value (0.3-0.4 D) which has been found for the analogous dioxane (15, p. 299).

However, this low moment cannot be explained either by a chair or a completely flexible conformation in view of the observed moment of dimethyl sulphide (15, p. 303). On the other hand the low moment can be rationalized in terms of a limited flexibility in

Substance	Solvent	Temp. (°C)	δε/δω	$\delta ec{V}/\delta \omega$	€ extrap.	ϵ solvent	V extrap.	$V_{ m solvent}$	$\Pr_{(\mathrm{cc})}^{P_{\mathrm{T}}}$	MR _D addv.	$P_{\mathbf{D}}$	D) Dr
 1,4-Dimethylenecyclohexane Bis-isopropylidenecyclohexane 	Benzene Benzene Benzene CCI4	20^{+20}_{-20}	$\begin{array}{c} -0.10\\ -0.09\\ -0.08\\ 0.22\end{array}$	$\begin{array}{c} 0.087 \\ 0.084 \\ 0.082 \\ +0.512 \end{array}$	$\begin{array}{c} 2.2825\\ 2.2620\\ 2.2421\\ 2.2384\end{array}$	$\begin{array}{c} 2.2826\\ 2.2623\\ 2.2422\\ 2.22384\end{array}$	$\begin{array}{c}1.13791\\1.15186\\1.16626\\0.62695\end{array}$	$\begin{array}{c}1.13808\\1.15190\\1.16624\\0.62694\end{array}$	$\begin{array}{c} 37.6\\ 37.7\\ 38.0\\ 58.4\end{array}$	$\begin{array}{c} 36.0 \\ 36.0 \\ 36.0 \\ 54.7 \end{array}$	$\begin{array}{c} 36.9 \\ 36.9 \\ 36.9 \\ 58.0 \\ \end{array}$	$\begin{array}{c} 0-0.1\\ 0-0.1\\ 0-0.1\\ 0\end{array}$
 (3) Bis-diphenylmethylidene- cyclohexane (4) 2,5-Diphenyldithiin (5) 1,4-Dithiane 	CS ₂ Benzene Dioxane Dioxane	22222	$\begin{array}{c} 0 & 0.02 \\ 0 & 40 \\ 0 & 40 \\ 0 & 0 \\ 0 $	+0.098 0.360 0.135 0.126 0.126	$\begin{array}{c} 2.6455\\ 2.2829\\ 2.2245\\ 2.2245\\ 2.2061\\ 0.101\\ 0.101\\ \end{array}$	$\begin{array}{c} 2.6456\\ 2.2830\\ 2.2246\\ 2.2246\\ 2.2062\\ 1.816\\ 1.816\\ 1.816\\ \end{array}$	$\begin{array}{c} 0.78128\\ 1.13830\\ 0.96740\\ 0.97838\\ 0.97838\\ 0.00007\end{array}$	$\begin{array}{c} 0.79130 \\ 1.13830 \\ 0.96740 \\ 0.97838 \\ 0.97838 \\ 0.08087 \\ 0.08087 \end{array}$	$129.4 \\ 145.3 \\ 36.8 \\ 37.4 \\ 27.5 \\ 129.5 \\$	133.0 71.4 32.6	$\begin{array}{c} 126\\79.5\\31.4\end{array}$	$\begin{array}{c} 0.4 \\ 1.77 \\ 0.51 \\ 0.54 \\ 0.56 \end{array}$
(6) <i>trans</i> -1,4-Dithiane-1,4-dioxide, m.p. 280° (7) <i>ci</i> s-1 4.Dithiane-1 4-diovide	Dioxane	40 40	06.0	0.50	2.1918 2.1918	2.1920	0.98990	0.98990	44.3		40.0	0.4
 (8) 1,4-Dithiane-1-monoxide (9) Dimethyl sulphoxide 	Dioxane Dioxane Benzene	$^{40}_{20}$	$\begin{array}{c} 17.4\\9.50\\21.81\end{array}$	$\begin{array}{c} 0.46 \\ 0.31 \\ 0.260 \end{array}$	$\begin{array}{c} 2.1918 \\ 2.1918 \\ 2.2830 \end{array}$	$\begin{array}{c} 2.1920\\ 2.1920\\ 2.2840\end{array}$	$\begin{array}{c} 0.98992\\ 0.98991\\ 1.13800 \end{array}$	$\begin{array}{c} 0.98990\\ 0.98990\\ 1.13808 \end{array}$	$\begin{array}{c} 469.7 \\ 244.7 \\ 337.5 \end{array}$		$\begin{array}{c} 40.6 \\ 35.9 \\ 20.1^{*} \end{array}$	$\begin{array}{c} 4.66 \\ 3.25 \\ 3.88 \end{array}$
*Calculated from refractive index and de	isity.		-									

TABLE II

Orientation polarization measurements

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which the molecule is largely in the "stretched" modes (II). In this connection it should be noted that unlike the isocyclic cyclohexane there will be two possibilities of "stretched" mode in dithiane of which the one where the hetero atoms tend toward the median positions should be more probable than the one where carbon rather than the sulphur occupies this median position. That is to say, II*a* is more probable than II*b*. Since the moment of II*a* would essentially be zero one must postulate on this basis that dithiane is flexible with an unequal conformational distribution favoring II*a*.

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Flexibility involving a frequency greater than the reading rate of an n.m.r. measurement is indicated by a single proton absorption for dithiane at room temperature. Confirmation of this evidence would be afforded if the flexible oscillation could be decreased at low temperature to an extent that it would be slower than the 116 c.p.s. downfield which Dr. S. S. Danyluk of this department has found at room temperature. When he cooled a 5% solution of dithiane to -120° in the 1:1 volume mixture of thionyl chloride – carbon disulphide (f.p. ca. -140°) he did not observe a splitting of the proton absorption band, but the marked broadening of this line toward virtual disappearance against the background at -120° is a strong indication of the complex spectrum to be expected at a relatively low oscillation rate. On balance of evidence the flexible form of dithiane is favored.

A contrasting rigidity in a six-membered ring is shown by the moment (Table II) of 2,5-diphenyldithiin. There is no possibility of a flexible form of this 1,4-dithiadiene; it must exist as a chair or boat. The observed moment (1.8 D) shows that the molecule has boat shape. If comparison with the moment of ethylene sulphide is valid (15, p. 299) the ethylene linkages in diphenyldithiin are not significantly distorted.

According to the X-ray diffraction analysis of March the C—S—C bond angle in 1,4-dithiane is 93°. This wide divergence from the 120° angle, which heretofore has seemed to characterize the flexible ring conformation, actually does not preclude flexibility. It is evident from geometry that the carbon atom in the ring is properly spaced for flexible behavior because of the greater bond length of C—S (1.81 Å) over that of C—C (1.51 Å) or C—N (1.46 Å) in exo-unsaturated cyclohexanes or piperazines. The equivalent angle in terms of the latter types would be about 115°.

According to Shearer the C—S—C bond angle in *trans*-1,4-dithiane-1,4-dioxide is 98°, which with the C—S bond length of 1.81 Å is practically equivalent to the 120° angle in exo-unsaturated cyclohexanes or piperazines. Therefore, on geometric grounds the flexible conformation is not excluded for dithiane dioxides in solutions, even though Shearer considers the trans isomers to be of chair conformation in the crystal.

It should be stressed that flexibility if it exists in the dithiane oxides is a consequence of favorable geometry due to the long C—S—C bond and not to inversion-oscillation which is characteristic of the C—N—C linkage. This is obvious in the fact that amines cannot be isolated as enantiomeric individuals because of inversion whereas the sulphoxides are configurationally stable.

In order to make a conformational evaluation from electric moment data the moment angle must be correlated with bond angle. In a substance such as 1,4-dimethylpiperazine the moment must evidently arise between the nitrogen nucleus and the non-bonded electrons of this atom. We presume that the non-bonded electrons in sulphoxides contribute little to the moment. If the contribution were appreciable the moments of *cis*- and *trans*-dithiane dioxides would not be so different as Table II shows them to be. The principal contribution must be due to the polar $S \rightarrow O$ linkage and we assume that its

bond angle is approximately the same as the moment angle. The C—S \rightarrow O bond angle has been specified as 107° by Shearer so the ==C₂==S \rightarrow O bond angle may be taken as 110°.

If dimethyl sulphoxide of moment 3.88 D is compared with 1,4-dithiane-1-oxide it is evident that the cyclic compound cannot exist in the flexible conformation because the mean value of the moments calculated for the extreme conformers would exceed the moment of dimethyl sulphoxide in benzene. Actually the observed moment of dithiane monoxide (in dioxane, which tends to enhance the apparent moment in benzene) is 0.63 D lower than that of dimethyl sulphoxide. This moment could be due only to a rigid "stretched form" or to a chair form, and the latter is energetically more probable.

Thus the chair conformation is assigned to the monoxide but a different situation may exist in the case of dioxides. Assuming that the bond angle $=C_2=S \rightarrow O$ and the moment angle are identically 110° the moment of the trans dioxide ought to be zero while the cis isomer ought to have a moment of 6.36 D.

The observed moment for the trans isomers apparently is 0.4 D, but this value is too low to be significant. Great precision and accuracy are necessary in order to attach any meaning to an apparent moment less than 0.5 D, and the trans dioxide because of its low solubility therefore is precluded. Because of this low solubility we have been unable to determine the n.m.r. spectrum in a suitable medium. Therefore it seems best to leave the question of *trans*-dithiane dioxide conformation in abeyance.

On the other hand the cis isomer is amenable for consideration. Clearly with an observed moment of 4.66 D *cis*-1,4-dithiane-1,4-dioxide cannot exist in a fixed chair conformation which should have a moment of 6.36 D. Alternatively with postulation of a flexible ring a calculation by the method of Hazebroek and Oosterhoff (2) has been made. If the observed moment of dimethyl sulphoxide is used as the group moment for $=C_2=S\rightarrow O$ (as before) then at a moment angle of 110° the μ of the cis isomer may vary from 0 to 7.36 D. The upper limit is sterically improbable because it represents the extreme boat form in which the oxygen atoms would overlap. The moment will therefore be comprised of three other "boat" aspects plus the stretched forms which are intermediate. The resultant is approximate to the observed moment of 4.66 D on the basis of equal contributions. While this assumption is unwarranted it does give reasonable agreement which is impossible for the chair conformation. Consequently the dynamic structure of limited flexibility is assigned to *cis*-1,4-dithiane-1,4-dioxide.

EXPERIMENTAL¹

1,4-Dimethylenecyclohexane

Into the top of a quartz tube 600×30 mm packed with 0.2–1.0 cm² Vycor chips in the region 140 mm to 440 mm from the top and heated externally to show a temperature of 510° to a centrally located thermocouple was added at a rate of 100 g/hr a total of 1040 g (4.56 mole) of a cis-trans mixture of 1,4-bisacetoxymethylcyclohexane. During this time a 50 cc/min stream of dry 99.8% nitrogen was passed downward through the pyrolysis tube and the dry, ice-chilled receiver which was connected to it. The top of the chip bed acted as a vaporizer for the diacetate.

A solution of the pyrolyzate in ether was water-washed to remove acetic acid (336 g, 61% according to titration) then dried by means of magnesium sulphate and distilled, finally through a Vigreux column at 20 mm Hg pressure to give 265 g, b.p. 28–75°. The chilled residue yielded 111 g, m.p. 65–72°, chiefly unchanged diacetate. The remainder was discarded.

The distillate, b.p. 28–75°, was fractionated through a 40-plate helix-packed column (r.r. 20:1 at 750 mm) to give a series of fractions which were complex according to gas chromatography; only toluene and xylene were identified besides the principal fraction (103 g, $n_{D^{20}}$ 1.4727, boiling at 122–123°, 750 mm). This crude 1,4-dimethylenecyclohexane, m.p. -32° to -27° , absorbed slightly (E_{max} , 87) at 230 m μ so it was treated with 50-mg portions of diethyl azodicarboxylate until the color of the latter persisted for 8 hours. The volatile fraction was removed under reduced pressure and then was distilled at 750 mm, yield 90.5 g, b.p.

¹Melting points have been checked against reliable standards.

121–122°, n_{D}^{20} 1.4717, d_{4}^{20} 0.821, capillary m.p. -28 to -26.5°. This pure material (single peak, retention time 16 minutes by gas chromatography on 20% carbowax firebrick) was transparent down to 215 m μ in methanol. Anal. Calc. for C₈H₁₂: C, 88.9; H, 11.2. Found: C, 88.9; H, 11.0. The infrared absorptions in carbon tetrachloride in cm⁻¹ (E_{max}) are 3075 (54), 2930 (118), 2840 (73), 1780 (19), 1655 (100), 1440 (79), 1400 (34), 1315 (36), 1180 (25), 1160 (49), 980 (21), 893 (402), 692 (105) in carbon tetrachloride. An additional peak at 785 (54) was found in carbon disulphide or in an undiluted sample but no further absorption out to 300 cm⁻¹. Slight differences from the spectrum in carbon tetrachloride were found for the neat sample, i.e. 2940 vs. 2930, 1455 (new, shoulder), 1165 vs. 1160, 982 vs. 980, and 888 vs. 893.

The nuclear magnetic resonance spectrum (60 Mc) of an undiluted sample showed two simple peaks. The peak characteristics of the four methylene hydrogens at 20 c.p.s. included half of the area under the peak at 107 c.p.s. characteristic of the eight ring hydrogens. Neither peak showed any tendency toward splitting when the temperature of a carbon disulphide solution was lowered to -120° C.

Bis-1,4-bromomethyl-1,4-bromocyclohexane

To a solution of 10.8 g (0.1 mole) of 1,4-dimethylenecyclohexane in 100 ml of diethyl ether and 2 ml of amyl alcohol containing 10 mg of diphenylamine (to favor homopolar addition) was added bromine at -40° C until the color was permanent. After solvent evaporation the product was crystallized from commercial hexane – diethyl ether (2:1) to give 29.8 g (69%), m.p. 134–135°. Anal. Calc. for C₈H₁₂Br₄: C, 22.5; H, 2.83. Found: C, 22.4; H, 2.78.

This tetrabromide (12.8 g, 0.03 mole) was dissolved in 200 ml of dry diethyl ether and stirred under nitrogen with 1.5 g (0.062 g-atom) of Grignard-quality magnesium plus a grain of iodine for 10 minutes and then was refluxed for 1 hour. The supernatant phase, waterwashed and magnesium sulphate dried, was distilled, finally at 121°, yield 1.3 g (40%) with negligible residue. This 1,4-dimethylenecyclohexane was transparent down to 215 m μ and gave a single gas chromatograph peak. Addition of bromine as described above gave a 62% yield of tetrabromide, m.p. 133.5–135°, not depressed by admixture with the original.

1,4-Cyclohexanedione

A solution of 0.546 g (0.005 mole) of 1,4-dimethylenecyclohexane in 20 ml of carbon tetrachloride was saturated with 5% ozonized oxygen at -10° . After vacuum evaporation of the solvent the residue was heated with powdered zinc and water at 90° for 90 minutes and then was steam-distilled. The distillate, treated with dimedone, gave the formaldehyde derivative, 0.885 g (30%), m.p. 188–189°.

The steam distillation residue was exhaustively extracted with petroleum ether (b.p. $40-60^{\circ}$). Evaporation of this extract left 0.22 g (39%) of 1,4-cyclohexanedione, m.p. 74°. After three sublimations the melting point, 78.4°, was not depressed by admixture with an authentic sample. The 2,4-dinitrophenylhydrazone melted at 237° (lit 240°).

The n.m.r. spectrum of a methylene dichloride solution of the cyclohexanedione showed only a single peak for all ring hydrogens at 88 c.p.s.

Bis-1,4-chloromercurimethyl-1,4-methoxycyclohexane

To a stirred suspension of 63.6 g (0.2 mole) of crystallized mercuric acetate in 400 ml of pure methanol was added 10.8 g (0.1 mole) of 1,4-dimethylenecyclohexane at room temperature. After 35 minutes the suspension showed a negative test for mercuric ion and was cooled to 0° and poured into a stirred solution of 12.2 g (0.21 mole) of sodium chloride in 400 ml of water. After 20 minutes the precipitate was filtered and washed with a little cold methanol, yield 63 g (98%). This crude product was extracted with 4 liters of boiling chloroform, leaving 15.7 g, m.p. 196-200°. Vacuum evaporation of the extract gave a first fraction (12.0 g, m.p. 170-190° (decomp.)) and then a second (32.5 g, m.p. 166-180° (decomp.)). Crystallization with recombination from hot acetone, chloroform, methanol, and dioxane separated the mercurial into its two geoisomers; A, 21 g, decomp. 217°, slightly soluble in hot chloroform, fairly soluble only in hot dioxane. Anal. Calc. for C10H18O2Hg2Cl2: C, 18.7; H, 2.87. Found: C, 18.7; H, 3.01. The infrared spectrum in potassium bromide (cm⁻¹) is 2950 (s), 2900 (s), 1460 (shld., m), 1450 (shld., m), 1443 (m), 1425 (m), 1405 (m), 1360 (m), 1312 (w), 1280 (m), 1243 (s), 1193 (w), 1166 (w), 1145 (m), 1110 (s) ,1090 (s), 1075 (shld., s), 1063 (s), 1042 (shld.), 963 (w), 912 (m), 886 (m), 860 (s), 763 (w), 755 (w), 709 (w). Geoisomer B, 24 g, decomp. 193°, is soluble in cold dioxane and easily soluble in hot methanol or chloroform. Anal. Calc. for C10H18O2Hg2Cl2: C, 18.7; H, 2.87. Found: C, 18.8; H, 3.07. The infrared spectrum in potassium bromide (cm⁻¹) is 2940 (s), 2840 (shld., m), 1460 (shld., m), 1450 (m), 1430 (m), 1405 (m), 1360 (w), 1340 (w), 1318 (w), 1275 (m), 1255 (m), 1185 (shld., m), 1140 (s), 1060 (s), 1025 (m), 970 (m), 943 (w), 904 (m), 865 (m), 746 (s), 703 (w), 663 (w).

When 18 g of geoisomer A (0.028 mole, decomp. 216°) was suspended in 30 ml of pure *n*-hexane and stirred vigorously with 4.8 ml (0.06 mole) of conc. hydrochloric acid for 5 minutes a residue was still undissolved. However, the hexane layer was separated, washed with water, dried with magnesium sulphate, and distilled to give a slight first fraction boiling up to 121° and then 1.6 g (53%) b.p. 121–122°. The distillation residue weighed 0.6 g (20% also calculated as dimethylenecyclohexane), was unsaturated, and showed ultraviolet peaks at 271, 260, and 253 m μ . The 1.6-g portion, n_D^{20} 1.4721, melted at -28° to -26.5° , m.m.p. not depressed with 1,4-dimethylenecyclohexane. The aqueous layer on treatment with alkali gave 11.5 g (95%) of mercuric oxide.

Polymerization of 1,4-Dimethylenecyclohexane

(a) By Ultraviolet (Broad Peak at 360 $m\mu$)

When the pure substance in a soft glass tube at $+35^{\circ}$ was irradiated for 14 days a yellow coating developed on the wall. The remaining liquid, distilled, contained 47% of unchanged dimethylenecyclohexane and also 16% (calc. as monomer) non-volatile syrup insoluble in methanol, benzene, and carbon tetrachloride with infrared spectrum (KBr pellet) in cm⁻¹: 3075 (vw), 2950 (s), 2850 (m), 1720 (s), 1658 (m), 1435 (s), 1165 (s), 887 (m). The solid material on the wall (12%) is a hard thermoplastic insoluble in carbon tetrachloride, methanol, benzene, and hexane with infrared spectrum in cm⁻¹: 2950 (s), 1720 (s), 1640 (s), 1440 (s), 1165 (s), 887 (s).

(b) By Benzoyl Peroxide

A 20% solution of dimethylenecyclohexane in dry benzene was refluxed for 3 days while 0.5 wt% portions of benzoyl peroxide were added at 10-hour intervals. The entire volatile portion was vacuum evaporated to a syrup which was washed with alkali and with water and dried at 100° (10 mm). The remainder (9%) is thermoplastic and soluble in carbon tetrachloride. The infrared spectrum, KBr pellet, in cm⁻¹, is 2950 (s), 1630 (m), 1443 (m), 1265 (s), 887 (w), 785 (m), 710 (m).

(c) By Aluminum Chloride

A violent reaction occurred when 1 g of the exo diene was treated with 0.5 g of freshly ground aluminum chloride. The carbon tetrachloride extract when washed with water and precipitated by 10-fold dilution with methanol gave 0.3 g of a brown thermoplastic solid, infrared absorption in KBr (cm^{-1}): 2950 (s), 2325 (w), 1620 (s), 1450 (s), 1370 (m), 785 (s), 740 (m). After the aluminum chloride was washed from the carbon tetrachloride insoluble residue there remained 0.2 g of a brown thermoplastic solid. By contrast no reaction of the exo diene occurred when it was treated with a solution of aluminum chloride in carbon tetrachloride.

Aromatization of 1,4-Dimethylenecyclohexane

When a 4.3 g of the exo diene was carried by nitrogen (25 cc/min) through a 15 mm dia. Vycor chip bed 5 cm long at 700-750° C the recovered material (70 wt%) was a mixture of benzene, toluene, and xylene in ratio 1:2:1 according to retention times on a carbowax-celite column at 140°. The collected fractions were identified by their ultraviolet and infrared spectra.

Isomerization of 1,4-Dimethylenecyclohexane

A solution of 7.7 g (0.07 mole) of the exo diene in 100 ml of peroxide-free dioxane plus 0.6 ml of 66 wt% aqueous sulphuric acid was refluxed for 3 hours and let stand for 8 hours more. The ethyl ether extract of the water-diluted system, washed acid free and dried by means of magnesium sulphate, was found to distill as follows: 1 g, 126–133° C; 2 g, 133–135° C ($n_{D^{20}}$ 1.4745); 0.7 g, 135–136° C ($n_{D^{20}}$ 1.4730); 2 g, 136–140° C; 0.2 g, 140–141° C; residue 0.7 g. All fractions showed olefinic unsaturation.

A solution of 0.54 g (0.005 mole as 1,4-dimethyl-1,3-cyclohexanediene) of the fraction b.p. $135-136^{\circ}$ in 15 ml of absolute ethanol was treated with 6% ozonized oxygen at -40° to saturation and then at -10° , again to saturation. Then the system was treated with aqueous sodium borohydride until oxidizing agents were absent. The solution was acidified with dilute sulphuric acid, then treated with an acid solution of 2,4-dinitrophenylhydrazine. After 2 hours the precipitate was filtered off, 0.45 g after washing with ethanol, m.p. 235-245°, and was crystallized from *p*-xylene, 0.3-g (13%), m.p. 254-256°. A mixture melting point with the derivative of acetonylacetone (m.p. 257°) was not depressed, thus indicating the presence originally of 1,4-dimethyl-1,3-cyclohexadiene.

cis-1,4-Bis-isopropylolcyclohexane

To a magnesium-free methyl chloride Grignard reagent prepared from 2.1 g-atom of the metal in 1200 ml of diethyl ether (yield 69% by titration) was added 60 g (0.3 mole) of dimethyl 1,4-cyclohexanedicarboxylate (largely cis isomer, m.p. 0°) in 60 ml of diethyl ether at a rate sufficient to maintain reflux with the vessel being ice-cooled (1 hour). After 20 minutes of subsequent reflux the cooled system was poured into cold, stirred, saturated aqueous ammonium chloride. After 10 hours the system was filtered to remove scum and both the residue and the aqueous phase of the filtrate were extracted with diethyl ether. All of the ethereal portions, dried with magnesium sulphate, were evaporated, leaving a magma from which was filtered 32 g (49%) of the glycol, m.p. 110–112°. Crystallization from benzene – carbon tetrachloride (1:2 by volume) raised the melting point to 115.5–116.5°. Anal. Calc. for $C_{12}H_{24}O_2$: C, 72.0; H, 12.1. Found: C, 72.1; H, 12.1. The infrared spectrum (KBr pellet) in cm⁻¹ is 3320 (s), 2975 (s), 2950 (s), 2860 (m), 1450 (m), 1445 (m), 1365 (s), 1355 (s), 1295 (w), 1230 (m), 1220 (m), 1155 (s), 1125 (s), 1105 (w), 945 (w), 935 (w), 912 (w), 898 (w), 872 (w), 830 (w), 808 (w), 780 (w); in chloroform solution 3550 (m), 3425 (m), 2940 (s), 2850 (s), 1460 (m), 1440 (m), 1380 (s), 1360 (s), 1320 (m), 1155 (s), 1125 (s), 940 (m), 905 (s), 870 (w), 840 (w).

trans-1,4-Bis-isopropylolcyclohexane

The cis glycol (4 g, 0.02 mole) was heated for 40 minutes with 8 g of anhydrous copper(II) sulphate at 130°. The system was then extracted with cold carbon tetrachloride to remove dehydration products, and subsequently with the same solvent hot. When the hot extract was cooled 0.8 g (20%) of trans isomer, m.p. 157–158°, crystallized out. Anal. Calc. for $C_{12}H_{24}O_2$: C, 72.0; H, 12.1. Found: C, 72.0; H, 12.1. The infrared spectrum (KBr pellet) showed absorption peaks at 2975 (s), 2950 (s), 2860 (m), 1445 (m), 1370 (s), 1360 (s),

1305 (w), 1240 (m), 1225 (m), 1160 (m), 1130 (s), 1120 (s), 945 (s), 915 (s), 872 (m), 783 (w); in chloroform solution 3550 (w), 3400 (w), 2900 (s), 2850 (s), 1460 (m), 1440 (m), 1370 (s), 1360 (s), 1320 (w), 1285 (w), 1135 (s), 938 (w), 908 (s), 868 (w).

1.4-Bis-isopropylidenecyclohexane

The substance may be dehydrated over alumina at 300° but better yields were obtained using formic acid. A solution of 10 g of the cis diol (0.05 mole) in 5 ml of formic acid was heated at 90–100° until a second phase separated after 5 minutes. The non-aqueous layer in diethyl ether was water-washed until it was neutral. Vacuum evaporation of the ether left 7.3 g (90% calc. as diene) which was dissolved in 5 ml acetone. Needles separated at -80° C, 2.1 g (26%), m.p. 70–71° C, which upon crystallization from acetone, methanol and subsequent sublimation melted at 78.5–79.5° C. Anal. Calc. for $C_{12}H_{20}$: C, 87.7; H, 12.3. Found: C, 87.6; H, 12.4. This 1,4-bis-isopropylidenecyclohexane forms a tetrabromide, m.p. 205–206°, after crystallization from commercial hexane. Anal. Calc. for $C_{12}H_{20}Br_4$: C, 29.8; H, 4.17. Found: C, 29.2; H, 3.76. The 1,4-diene is transparent in the ultraviolet down to 210 m μ but absorbs strongly at shorter wavelengths. The infrared spectrum (KBr pellet) in cm⁻¹ is 2930, 2850 (s), 28 (s), 1615 (w), 1430 (s), 1370 (shld., m), 1360 (s), 1195 (s), 1115 (w), 1095 (w), 970 (w).

The mother liquors from crystallization of the diene contained 5.6 g, b.p. 83–115° (10 mm). This oil absorbs at 281, 250, and 243 m μ and it slowly polymerizes.

1,4-Bis-diphenylmethylidenecyclohexane

To a magnesium-free Grignard reagent prepared from 1 mole of bromobenzene in 385 ml of diethyl ether was added a solution of 30 g (0.015 mole) of dimethyl 1,4-cyclohexanedicarboxylate (chiefly cis) in 60 ml of ether during 1 hour. After 20 minutes of subsequent reflux the system was poured into 300 ml of glacial acetic acid. After the addition of 2 ml of hydrochloric acid the solution was boiled for 5 minutes, cooled, and filtered, 23.4 g (91%). This diene was crystallized from dioxane (150 ml/g), m.p. 257–259°. It is also soluble in hot benzene, toluene, and carbon tetrachloride but is almost insoluble in methanol or ethanol. A dioxane solution absorbs in the ultraviolet at 246 m μ (E_{max} 27,000) comparable with the absorption by benzophenone at 250 m μ . The infrared spectrum (cm⁻¹, KBr pellet) is 3040 (m), 2950 (m), 2855 (m), 2825 (m), 1620 (w), 1590 (m), 1475 (s), 1460 (w), 1430 (s), 1210 (m), 1070 (m), 1030 (w), 995 (w), 980 (m), 915 (w), 880 (w), 765 (s), 755 (s), 730 (s), 697 (vs), 673 (w).

The substance shows strong green fluorescence in ultraviolet light but becomes permanently yellow after this irradiation. In carbon tetrachloride solution aerated with oxygen under ultraviolet irradiation the yellow color appears within 2 hours. The melting point of the recovered solid has decreased to $248-254^{\circ}$. In absence of light, ozonization in carbon tetrachloride does not produce a color change; the ozonide yields benzophenone (42%).

Electrical Measurements

The dielectric constants of the crystalline substances were determined by the method previously described (8, 9). The results of Table I have been calculated from the extrapolations shown in Fig. 1. All wafers were prepared from the pure compounds except in the case of bis-diphenylmethylidenecyclohexane, where it was necessary to use 2% of polyethylene wax in order to effect consolidation. The dielectric constant was corrected for this dilution. The specific volumes and dielectric constants of solutions, from which the total polarizations and moments of the dithiane oxides of Table II are calculated, are shown in Fig. 3.



FIG. 3. Extrapolations of dielectric constant (ϵ) and specific volume (\overline{V}). A, A': *trans*-1,4-Dithiane-1,4-dioxide; B, B': dithiane monoxide; C, C': *cis*-1,4-dithiane-1,4-dioxide.

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