monomer is 0.733 cc./g. Thus in the region of interest, the protein specific volume is only 0.005 cc./g. greater than the probably dilute solution value for dimer albumin, whereas from the data of McMeekin it is 0.021 cc./g. greater for β-lactoglobulin.

The close agreement between the partial specific volume of dimer albumin in the "wet" crystal and its probable value in dilute solution appears to suggest that, in spite of the relative proximity of neighboring protein molecules, protein–protein interactions are not strong in the wet dimer albumin crystals. The crystals are certainly very soft. Stronger interactions should lead to harder crystals, as in β-lactoglobulin, and some concomitant changes in partial specific volume.

It is difficult to understand the physical significance of the actual values obtained by McMeekin for β-lactoglobulin. It would seem reasonable that the water first absorbed by the dry protein at low relative humidities should be attached to the charged groups on the side chains, with electrostriction causing a considerable shrinkage in the volume of protein plus water on a molecular level[21] (although this would not show up as appreciable changes in the macroscopic crystal volume for the reasons discussed above). The water bound at higher relative humidities is held by much weaker forces, the electrostriction being small or negligible, so that the partial specific volume of this water should be nearly that of the pure solvent. There are no obvious forces which could be responsible for the contraction in solvent volume observed for β-lactoglobulin. The discrepancy between the β-lactoglobulin and dimer albumin results, in this respect, points up the desirability of further studies of this type on a variety of crystalline proteins.

Acknowledgments.—We wish to thank Professor John T. Edsall for his stimulating interest at all stages of the work and during the preparation of this manuscript.

(21) A discussion of the significance and magnitude of electrostriction effects is given by E. J. Cohn and J. T. Edsall, in "Proteins, Amino Acids and Peptides," Reinhold Publ. Corp., New York, N. Y., 1943, Chap. 7, p. 155.

BOSTON 15, MASSACHUSETTS

[CONTRIBUTION FROM THE SPECTROSCOPY LABORATORY AND DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Vibrational Spectra and Possible Structures of the Dimers of Cycloöctatetraene[1]

BY R. C. LORD AND R. W. WALKER

RECEIVED NOVEMBER 20, 1953

Two dimers of cycloöctatetraene, one a liquid with two double bonds (m.p. 14°) and the other a solid with three double bonds (m.p. 43°), discovered by Reppe, Schlichting, Klager and Toepel, have been studied by means of infrared and Raman spectra. A 1:3 mixture of the dimers was produced by heating the monomer for some hours at 160°. Presence or absence of oxygen seemed to have little effect on this ratio, but the solid dimer was found to convert quantitatively to the liquid dimer on simple heating above 200°. Of the two structures proposed by Reppe and co-workers for the liquid dimer, one is supported by the spectroscopic evidence and the other seems definitely excluded. Two structures for the solid dimer are proposed, neither of which is entirely in accord with the observed spectra.

The dimerization of cycloöctatetraene was discovered by Reppe and his co-workers.[2] They reported the existence of two dimers, a solid melting at 43° and containing three double bonds, and a liquid containing two double bonds. Apart from boiling points at various low pressures, no other physical data on the dimers were given by them. Reppe, *et al.*, pointed out that the small number of double bonds in the dimers implies the formation of many new saturated rings, since no evidence for aromatic rings could be found. They also suggested that the dimers were formed by diene condensation through the intermediate of the bicyclo-[4.2.0]octa-2,4,7-triene isomer of cycloöctatetraene. Two structures suggested by them for the liquid isomer (two double bonds) are shown in Fig. 1 (I and II). They suggested no structure for the solid dimer (three double bonds) because diene condensation of the bicycloöctatriene cannot result in an odd number of double bonds.

These proposed structures do not lend themselves readily to elucidation by either physical or chemical methods. It seemed worthwhile, however, to investigate the infrared and Raman spectra of the compounds, and to interpret the spectra in terms of the proposed and other plausible structures, with the objective of drawing as detailed conclusions as possible.

Reppe, *et al.*,[2] reported that only the liquid dimer is formed by dimerization in an atmosphere of nitrogen. We were unable to confirm this, and believe that their preparation of the pure liquid isomer under nitrogen resulted from the high temperature (230°) attained at one stage of the preparation. In our experience the ratio of liquid to solid dimer depended on the temperature of the dimerization rather than the presence or absence of oxygen. In the course of six dimerizations under different atmospheric conditions ranging from pure nitrogen to laboratory air, the solid:liquid dimer ratio (as shown by infrared spectra) was approximately constant at 3:1 as long as the temperature stayed at about 160°. However, if the dimerization was

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(1) Based on the thesis presented by R. W. Walker to the Graduate School of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1952.

(2) (a) W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948). (b) J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publ. Corp., New York, N. Y., 1949, pp. 210–212.

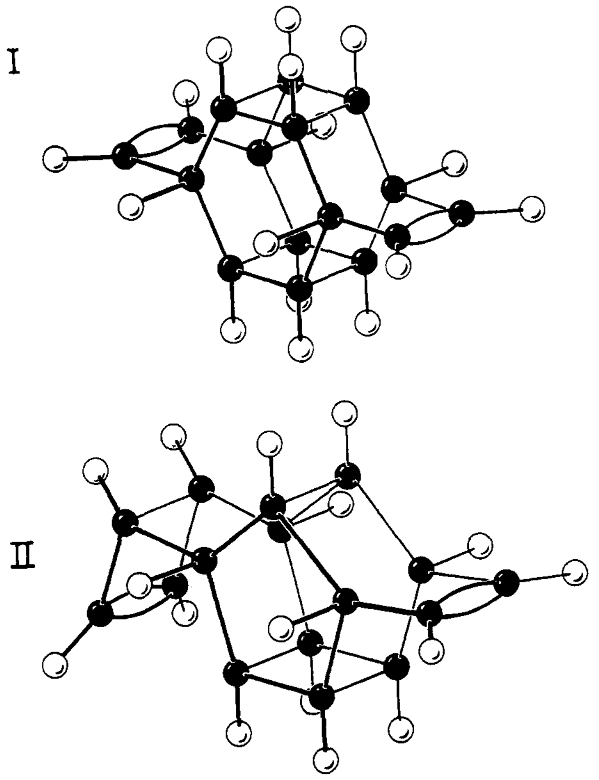

Fig. 1.—Possible structures of the dimer with two double bonds.

carried out above 200°, or if the pure solid was heated for some time at such temperatures, pure liquid dimer was obtained.

After the present work was completed Jones[3a] reported the isolation of a new solid dimer (m.p. 38.5°) containing two double bonds and yielding a solid (m.p. 44.5°) on complete hydrogenation. The circumstances under which Jones' solid dimer is produced (dimerization in a high-boiling solvent, for example) and the identical melting points of its silver nitrate adduct and of the principal adduct obtained from the liquid dimer, make it possible, as was emphasized by Jones, that the liquid dimer is chiefly his solid dimer with the melting point depressed by other compounds present to an amount of 5–10%. These other compounds are presumed by him to be Reppe's solid dimer (m.p. 43°) and the hydrogenated Jones dimer.

Jones' doubt about the existence of a pure liquid dimer is probably correct. However, the following facts needed a quantitative explanation before this conclusion can be accepted: 1. The melting point of the liquid dimer obtained in our work (14°) and its refractive index ($n^{25}\mathrm{D}$ 1.5842) are close to those reported by Jones (m.p. 13° and $n^{20}\mathrm{D}$ 1.5890) and by Reppe ($n^{20}\mathrm{D}$ 1.5856). If the liquid dimer is indeed a solid of depressed freezing point, it is remarkable that in three separate laboratories the nature and amount of impurity was so nearly the same that freezing points and indices of refraction agreed closely. 2. The infrared spectrum of the liquid dimer shows no evidence of the presence of Reppe's solid dimer. This fact is not completely indicative

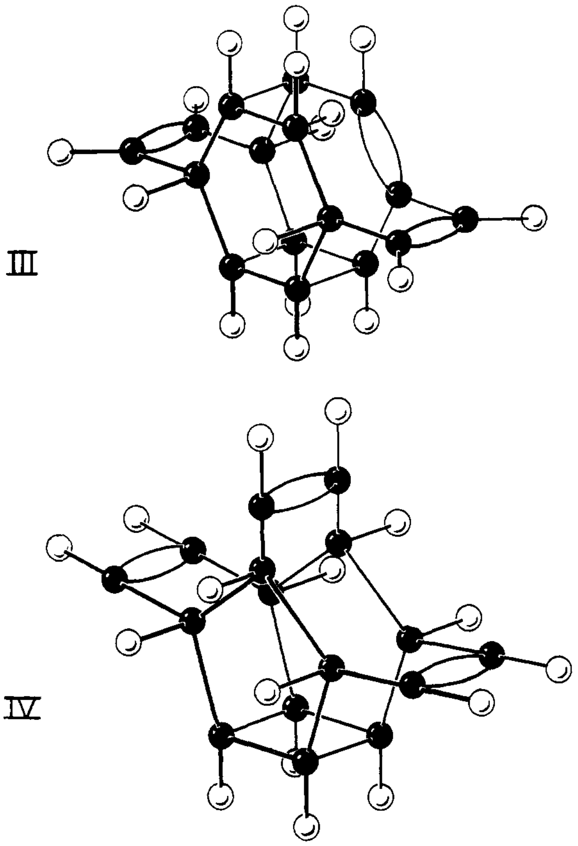

Fig. 2.—Possible structures of the dimer with three double bonds.

of the absence of the latter, because the analytical sensitivity of the spectrum under the conditions used in obtaining it was such that 2% of solid would have probably been undetected, and conceivably 1 or 2% more might have escaped notice. However, the spectrum of the liquid dimer (see Fig. 3) is markedly simple compared with that of the recrystallized solid dimer (Fig. 4) and indicates little impurity. 3 The hydrogenated liquid dimer obtained by us and by Reppe, *et al.*, showed a melting point of 34–36°, and the hydrogenated Jones dimer one of 44.5°. While this difference may also be ascribed to the impurities present in the liquid dimer, it is again remarkable that our figures and Reppe's agree so closely.

We have found evidence for another solid dimer (m.p. 53°) of which so little was obtained that we were unable to do chemical work with it, but did obtain an infrared spectrum. The spectrum shows clearly that it is neither the Reppe solid dimer nor the liquid and that it contains more than two double bonds, including one probably in a four-membered ring. It is highly unlikely that this material is to be identified with Jones' dimer, but may possibly be the intermediate dimer formed in the first *exo* step of the dimerization.[3b]

[3a] W. O. Jones, *J. Chem. Soc.*, 2036 (1953).

[3b] NOTE ADDED IN PROOF.—Through the courtesy of Dr. W. O. Jones, we have obtained a sample of his solid dimer. Its infrared spectrum agrees quite closely with that of the liquid dimer with respect to every strong band except the one at 805 cm.$^{-1}$, and to many weak bands. However the other weak bands, where disagreement occurs, and the 805 cm.$^{-1}$ band show that the liquid dimer contains some impurity. It is rather definite that the impurity is not the solid dimer

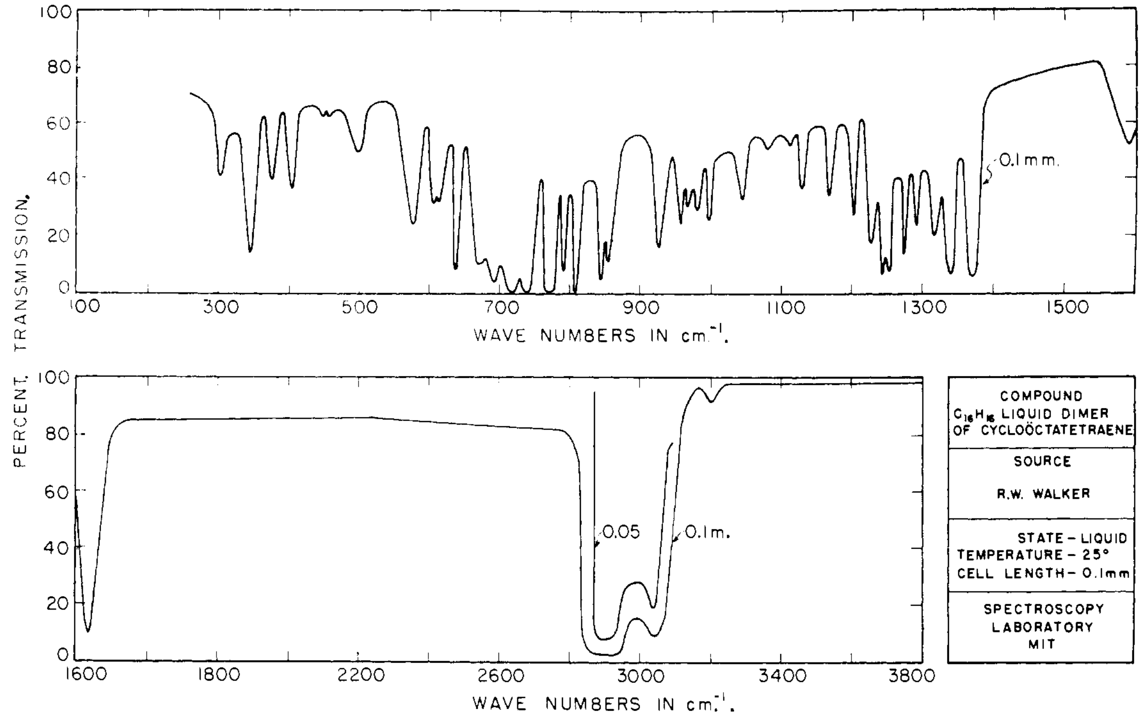

Fig. 3.—Infrared absorption spectrum of dimer with two double bonds.

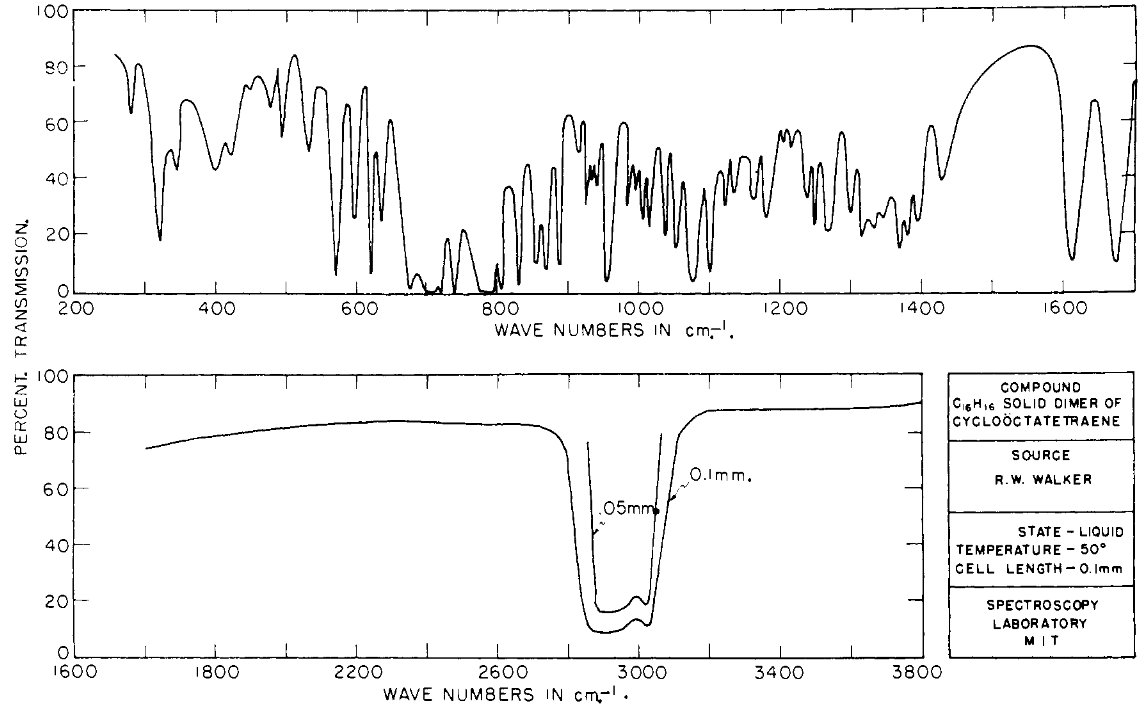

Fig. 4.—Infrared absorption spectrum of dimer with three double bonds.

Discussion of Spectra

The infrared and Raman spectra of the dimers and the infrared spectra of their hydrogenated products were investigated with previously described equipment and procedures of this Laboratory.[4] Spectroscopic results are given in Tables I

with three double bonds. The infrared spectrum of a partially hydrogenated sample of the latter, also obtained from Dr. Jones, showed clearly that the sample was a complex mixture of compounds in various stages of hydrogenation. The apparent break in the hydrogenation rate at a point corresponding to removal of two double bonds must result from some more complicated source than the clear-cut hydrogenation of two of the three double bonds.

(4) Raman spectra, including semi-quantitative depolarization measurements, were obtained with a Zeiss 3-prism instrument (R. C. Lord and E. Nielsen, *J. Chem. Phys.*, **19**, 1 (1951)). Sharp Raman lines are accurate to 1-2 cm.$^{-1}$ and diffuse ones to 3-5 cm.$^{-1}$. Infrared spectra were obtained over the spectral range 250-3800 cm.$^{-1}$ (650-3800 cm.$^{-1}$ for the hydrogenated dimers) with a modified Perkin-Elmer Model 12B instrument using prisms of CaF_2, NaCl,

and II and infrared curves are shown in Figs. 3–6. Visually estimated intensities are given for the Raman lines, and approximate depolarization factors for lines that were measurably polarized.

TABLE I

INFRARED AND RAMAN SPECTRA OF LIQUID DIMER

Infrared,		Raman,			Infrared,		Raman,		
Cm.$^{-1}$	*I*	Cm.$^{-1}$	*I*		Cm.$^{-1}$	*I*	Cm.$^{-1}$	*I*	
		3048	9	p	852	s			
3042	s				844	s			
2930	vs	2930	10	p	805	vs			
		1611	9	0.3			800	3	0.6
1606	s						794	1	
		1597	2	.3	787	s			
1588	m				765	vs	765	1	.5
		1382	1	.5			753	2	.4
1364	s				734	vs			
1335	s						721	7	.3
1331	m				716	vs			
1328	w				693	vs	693	1	.5
1311	m				674	s			
1292	m				639	s	635	1	
1274	m				613	m	609	2	
1250	s	1248	7		601	m			
1242	s				579	m			
1226	s						557	2	
1204	m	1203	1				527	2	.6
1168	w				508	m			
		1147	1		496	m	494	4	
1132	m				459	w	456	5	.65
1105	w	1108	5		449	w			
1080	w	1083	2				432	1	
1058	m				404	m			
		1033	1				395	5	
		1008	4		371	m			
993	m				342	s	343	1	
987	m						313	2	
965	m				308	m			
958	m						251	4	
922	m	924	4				231	4	
		909	3						
		857	4	0.5					

Two-double-bond Isomer.—The dimerization of cycloöctatetraene was presumed by Reppe, *et al.*,[2] to be a diene synthesis of the Diels–Alder type. They postulated that rearrangement of cycloöctatetraene to the 6,4-fused-ring isomer bicyclo[4.2.0]-octa-2,4,7-triene precedes the two-step Diels–Alder condensation. The two ways in which condensation can proceed are *exo,exo* and *exo,endo*. These two produce structures I and II of Fig. 1, respectively.[5]

TABLE II

INFRARED AND RAMAN SPECTRA OF SOLID DIMER

Infrared,		Raman,			Infrared,		Raman,		
Cm.$^{-1}$	*I*	Cm.$^{-1}$	*I*		Cm.$^{-1}$	*I*	Cm.$^{-1}$	*I*	
3035	s	3046	8	p	987	m	986	4	
2950	vs	3023	3		955	s	958	5	
		2931	10	p	940	m			
1736	w				932	m			
1675	s	1677	8	0.2	925	m			
1615	s	1617	8	.2	916	w	919	5	
1428	m	1427	6	.4	884	s	885	2	
1398	m	1400	4	.3	867	s			
1380	m				858	m	859	2	
1371	s	1367	3		835	s	836	3	0.4
1346	m				805	vs	808	3	.4
1336	m	1332	3		792	vs	794	3	.4
1316	m				740	s	739	3	.6
1298	m	1301	4		720	s	724	2	.3
1270	s	1272	4	0.7	702	vs	703	7	.3
1246	m	1244	4	.7	680	s			
1240	m				637	s	639	2	.2
1215	m	1215	6	.6	620	s	621	2	.4
1204	w				598	m	595	2	
1178	m				571	s	568	3	
1163	w				528	m	528	4	
1135	m	1136	4	0.5	497	m	495	6	0.3
1124	m				482	w	481	5	.4
1104	s	1107	1		451	w	449	2	.4
1090	s	1090	3		418	m	419	4	.6
1075	s	1076	3		399	m	399	4	.6
1055	m	1057	3		342	m	342	3	
1035	m	1038	4		321	s	324	3	0.5
1008	m	1010	3		284	w	286	25	.5
1002	m						246	3	.6
995	m						203	1	
							152	1	

If it is assumed that the structural problem is simply one of a decision between I and II, the vibrational spectra should furnish enough information to solve it. Structure I should have D_{2h} symmetry or approach it closely, whereas II would at most have a plane of symmetry. The infrared and Raman selection rules for the structures are summarized in Table III, together with a summary of the observed spectra.

TABLE III

SELECTION RULES FOR STRUCTURES I AND II

Spectroscopic activity	Predicted for I	Predicted for II	Obsd. for liq. dimer
Total Raman lines	45	90	33
Lines below 1700 cm.$^{-1}$	37	74	31
Polarized lines	14	45	13
Polarized below 1700	11	37	11
Infrared bands	35	90	46
Bands below 1700	28	74	44
Coincidences	0	90	14
Coincidences below 1700	0	74	12
Silent frequencies	10	0	..

It will be seen at once that neither structure agrees very closely with the observed spectra. This is hardly surprising for a molecule with ninety vibrational degrees of freedom, for which accidental degeneracies, failure of infrared selection rules in the liquid phase and other sources of disagreement may be anticipated. However, the over-all agreement is closer for I, especially with respect to frequencies below 1700 cm.$^{-1}$, which include all fundamentals except the sixteen C–H stretching vibrations. The excess of observed infrared bands can be attributed to our inability to distinguish rel-

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KBr and KRS-5 (R. C. Lord, R. S. McDonald and F. A. Miller, *J. Opt. Soc. Am.*, **42**, 149 (1952)). Band transmission minima are accurate to 1-2 cm.$^{-1}$ at wave numbers below 1700 cm.$^{-1}$. Thus infrared and Raman frequencies for the same vibration should agree within 2-3 cm.$^{-1}$ except above 1700 cm.$^{-1}$ or for broad or fuzzy bands. In all cases spectra were observed on samples in the liquid state, which of course required slightly elevated temperature for the dimer melting at 43° and for one of the hydrogenated materials.

(5) References 2a and 2b show the steps in the two processes.

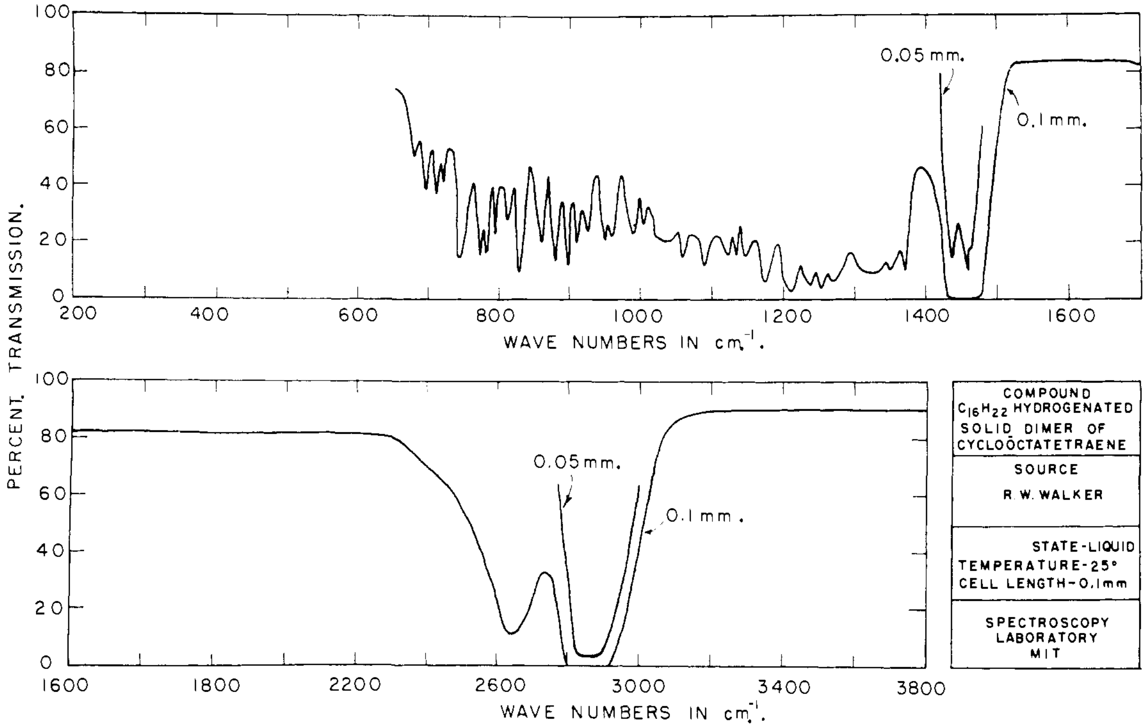

Fig. 5.—Infrared absorption spectrum of hydrogenated dimer $C_{16}H_{20}$.

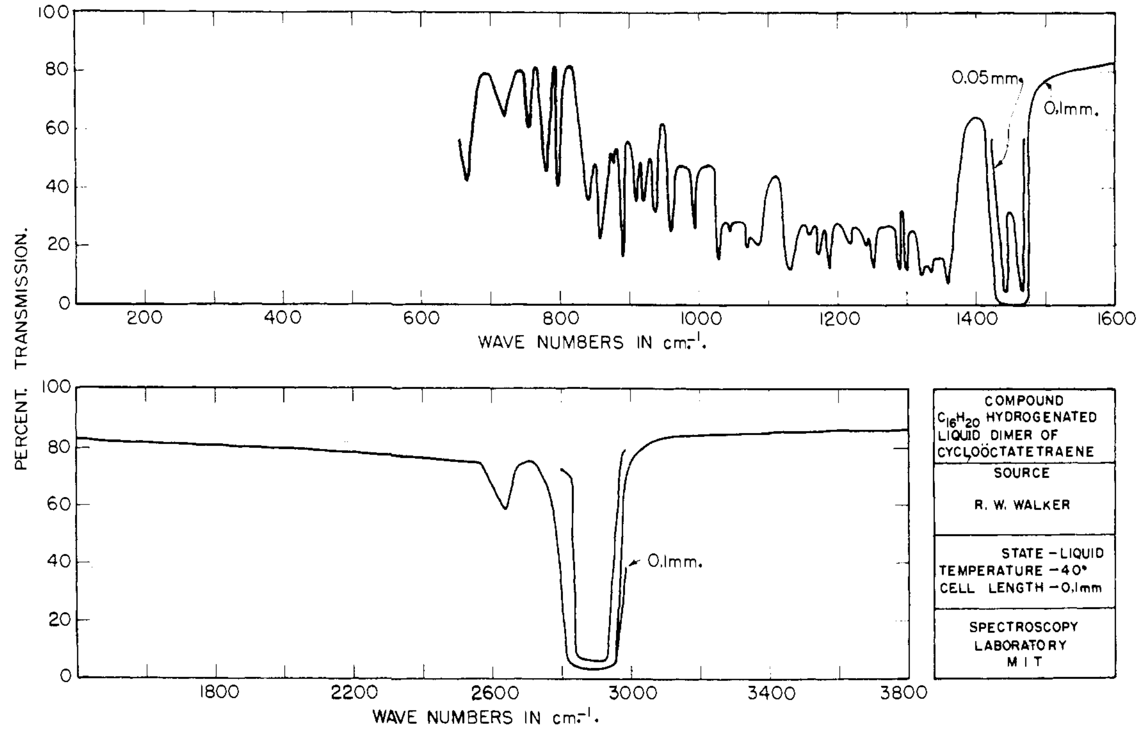

Fig. 6.—Infrared absorption spectrum of hydrogenated dimer $C_{16}H_{22}$.

atively strong overtones and forbidden fundamentals from weak allowed fundamentals.

The most serious disagreement between theory and experiment for structure I is the appearance of twelve coincidences below 1700 cm.$^{-1}$, where none is expected save by accident. It seems likely that many of these coincidences occur because two different modes of vibration, though belonging to different symmetry species (one infrared-active, the other Raman-active), are quite similar mechanically and hence have nearly identical frequencies. The double-bond vibrations (which we do not regard as coincidences) illustrate this point. The two double bonds are identical by symmetry in structure I. Two slightly different double-bond frequencies are expected, however, when the double bonds vibrate in phase (Raman-active) and out of phase (infrared-active). Because the coupling between the double bonds is extremely weak, the two frequencies will be very nearly the same. The observed double-bond frequencies are at 1606 in the infrared and 1611 in the Raman effect. This difference is regarded as too large to be experimental error, but is reasonable for two similar but uncoupled modes of vibration.[6]

It is to be expected that other kinds of vibration will behave similarly, and in view of the number of fundamentals below 1700 cm.$^{-1}$, twelve coincidences can plausibly be considered to originate in this way. In the spectrum of the three-double-bond isomer (Table II), every line observed in the Raman effect between 250 (the lower limit of the infrared measurements) and 1700 cm.$^{-1}$ coincides with an infrared band. The usual agreement is 3 cm.$^{-1}$ or better and the number of lines is more than forty. In view of the close chemical similarity of the two isomers, this difference in spectroscopic behavior is indicative of considerable difference in symmetry. If structure II, which has no symmetry, were correct for the liquid dimer, it would be expected to give a rich spectrum resembling that of the solid dimer in number of lines and coincidences. Therefore the simple spectrum of the liquid dimer favors structure I.

There is evidence of a different kind in favor of structure I. The double bond frequencies (1606 and 1611) are so close together that they could readily arise from two identical lightly-coupled double bonds. If so, each of these alone should have a characteristic frequency near 1609. It has been recognized for many years[7] that ring strain affects the value of the double-bond frequency. The nature of this effect is illustrated for some small ring compounds in Table IV. The frequency increases from 1566 in cyclobutene to 1650 (the normal olefinic value in *cis* compounds) in cyclohexene and larger rings. Fusion of a second ring introduces additional strain, so that a fused five-membered ring containing a double bond exhibits a lowered double-bond frequency (1568 in bicyclo[2.2.1]-heptene-2 compared with 1611 in cyclopentene). Similarly a double bond in a fused six-membered ring shows the frequency at 1614 (in bicyclo[2.2.1]-octene-2) rather than at 1646, as in cyclohexene. Strain also changes the olefinic C–H stretching frequency in a well-defined way, raising it from a normal 3017 in cyclohexene to 3045 in cyclopentene and 3060 in cyclobutene. Analogous changes are shown by the fused ring compounds. On the other hand, in compounds with more than two carbons attached to the olefinic double bonds, a marked elevation of the double-bond frequency is found. In 1-methylcyclopentene the frequency is raised nearly 50 cm.$^{-1}$ above that in cyclopentene. Similar but smaller increases occur in 1-methylcyclohexene and 1-methylcycloheptene (Table IV).

TABLE IV

DOUBLE-BOND FREQUENCIES IN RING COMPOUNDS

Cyclobutene	1566	Cycloheptene	1651
Bicycloheptene[a]	1568	1-Methylcyclopentene	1658
Cyclopentene	1611	1-Methylcyclohexene	1674
Bicycloöctene[b]	1614	1-Methylcycloheptene	1673
Cyclohexene	1646		

[a] Bicyclo[2.2.1]heptene-2. [b] Bicyclo[2.2.2]octene-2.

With the above results, elimination of structure II is possible and support for I is obtained. II contains two different double bonds, one in a fused six-membered ring and one in a fused four-membered ring. These should produce two distinct double-bond frequencies at identical positions in the Raman and infrared spectra, one near 1614 (observed) and one somewhat below 1566. No evidence of the latter is found. There should also be two distinct olefinic C–H stretching frequencies at about 3040 (observed) and 3060 (missing). The absence of the 1560 and 3060 frequencies is evidence against II and in accordance with expectation for I.

Thus many details of the observed spectra of the liquid dimer are consistent with the symmetrical structure I, the only serious problem being the coincidences discussed above. It seems unlikely that other structures (such as II) whose formation can be understood by presently known chemical reactions will be able to satisfy simultaneously the severe requirements of the chemical and spectroscopic results. Present evidence therefore supports structure I.

Three-double-bond Isomer.—Reppe, *et al.*,[2] proposed no structures for this isomer. Its formation was presumably believed by them to take place through some more complicated mechanism than a simple Diels–Alder diene synthesis, which under the circumstances could not lead to a product containing an odd number of double bonds. Perhaps their conclusion that oxygen is necessary for its formation, which we have found not to be the case, encouraged this point of view. The ease of conversion of the three-double-bond isomer to the other, a conversion that is not reversible in our experience, implies that the multiple-ring structures of the two dimers are not greatly dissimilar, and that any structure proposed for the three-double-bond isomer should enable one to understand the change to the other.

If structure I be taken as correct for the latter, it must represent a considerable part of the structure of the former. From the double-bond frequency at 1615 (Table II), at least one of the three double bonds is similar to those of structure I. The other double-bond frequency at 1675 is remarkably high and must involve some frequency-raising effect. Effects that might apply here are a *trans* structure,[8] substitution of carbon for hydrogen on the double-bond carbon atoms (Table IV), and large-angle strain.[9]

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(6) A disturbing feature of each spectrum is the presence of a satellite frequency near the double-bond fundamental. Each companion is low in frequency and intensity, and the one in the Raman effect is polarized. The separation from the fundamental differs in the two spectra. The frequencies are regarded as combination tones which acquire intensity by Fermi interaction with the fundamentals.

(7) See, for example, K. W. F. Kohlrausch and co-workers, *Ber.*, **69**, 729 (1936); **75**, 1385 (1942).

(8) *trans* frequencies usually lie 15–20 cm.$^{-1}$ higher than analogous *cis* frequencies. See N. Sheppard and D. M. Simpson, *Quart. Revs.*, **6**, 1 (1952).

(9) By large-angle strain is meant a strain that expands the C—C=C angle above its "normal" value of 120°. Such strain appears to raise the double-bond frequency just as strain decreasing the angle lowers it (Table IV). Presumably the frequency increase would

A *trans* double bond seems unlikely in view of the highly condensed nature of the dimer, but multiple carbon atoms on one of the double bonds would be a reasonable possibility. Migration of hydrogen would be required at some stage of the dimerization, which might take place in four steps: 1. addition of one bicyclo[4.2.0]octa-2,4,7-triene ring to another, as in the first "*exo*" step of the formation of structure I; 2. rupture of the C–C bond opposite the cyclobutene double bond; 3. migration of a hydrogen atom from a tertiary carbon atom adjacent to one of the atoms of the ruptured bond to the other, more remote atom, with the formation of a double bond between the adjacent atom and the tertiary carbon; 4. condensation of the cyclobutene ring with the six-membered ring of the other part of the dimer, as in the second "*exo*" step in the formation of structure I. These steps lead to structure III of Fig. 2, which could then be converted to I by migration of a hydrogen from the only CH_2 group back to the tertiary carbon from which it came, with subsequent closing of the four-membered ring.

The difficulties with III are that it has a double bond at a bridgehead, and that while its conversion to I can be understood if migration of hydrogen occurs, such migration is not expected, and renders the third step above doubtful. Without such a step, however, establishment of a tertiary carbon at a double bond is impossible.

In discussion of this problem with Professor J. D. Roberts, he suggested a structure (IV) that avoids these difficulties. If the dimerization can proceed not only by condensation of two molecules of bicyclo[4.2.0]octa-2,4,7-triene, but also by condensation of one of these with cycloöctatetraene, IV may result. This can take place if a tub form of cycloöctatetraene sits down on the triene in such a way that the cyclobutene double bond adds to carbon atoms 1 and 6, and the *para* carbon atoms of the six-membered ring join to atoms 2 and 5, of cycloöctatetraene.

Two of the three double bonds of IV thus arise from two opposite double bonds of cycloöctatetraene and the third from the six-ring of the triene. The latter becomes equivalent by symmetry to one of the former, and both should closely resemble the double bonds of I. This is in agreement with the spectra, for one of the two observed double-bond frequencies (1615) lies near those of the two-double-bond isomer, and the other (1675) might result from large-angle strain. Models of IV indicate that such strain would exist for the middle double bond.

Chemical evidence for IV lies chiefly in the report of Reppe, *et al.*,[2] confirmed by Jones,[3] that two of the three double bonds hydrogenate easily and the third much less readily.[3b] We also found indications of this distinction, but the difference in rates with our catalyst (reduced platinum oxide) did not appear to be sufficient to enable a clean preparation of the partially hydrogenated compound. Such a preparation would offer useful evidence for (or against) IV, since the infrared spectrum should show plainly which double bond remains. Mechanism of solid-to-liquid isomer conversion from IV to I could take place by rupture of the C–C bond at the top right-hand side of each five-membered ring, linkage of the central double-bond carbon atoms to the two adjacent to the right-hand double bond carbons, and closure of the four-membered ring. This mechanism is understandable in the light of similar rearrangements in small-ring compounds.

TABLE V

SELECTION RULES FOR STRUCTURES III AND IV

Spectroscopic activity	Predicted for III	Predicted for IV	Obsd. for solid dimer
Total Raman lines[a]	90	90	47
Lines below 1700 cm.$^{-1}$	74	74	45
Polarized lines	90	25	26
Polarized below 1700	74	20	24
Infrared bands[a]	90	69	60
Bands below 1700	74	56	58
Coincidences	90	69	47
Coincidences below 1700	74	56	45
Silent frequencies	0	0	..

[a] Raman lines and infrared bands that are undoubtedly multiple but have not been resolved are counted as single. The most obvious example of such multiplicity is the unresolved collection of C–H stretching frequencies near 2950 cm.$^{-1}$.

Structure IV would have more symmetry than III (probably C_{2v} *vs.* C_1) and the spectroscopic activities of the two would differ. They are given in Table V for these structures. It will be seen that neither structure agrees well with the observed spectra. As was the case with the liquid dimer, fewer lines are observed in all categories than are predicted except for polarized lines of structure IV. The most clear-cut feature of the selection rules on which differentiation between III and IV might be based is the number of Raman lines having coincidences in the infrared. IV should have 21 Raman frequencies, eight below 1700 cm.$^{-1}$, that are infrared active, whereas all frequencies should be active in both spectra for III. The observed spectra, in which all Raman lines are observed in the infrared, are therefore more consistent with III.

Although the number of polarized lines observed seems to agree somewhat better with IV, the semiquantitative method used for the polarization measurements is incapable of distinguishing between slightly polarized and depolarized lines. Thus the number of polarized lines observed is a lower limit, and actually is in disagreement with the number expected for IV. Thus on the basis of symmetry considerations alone, structure III is preferred over IV, but neither receives much support. This is no doubt to be expected when the molecule is large and neither structure has much symmetry.[10]

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continue the curve of frequency *vs.* angle that can be plotted from Table IV, but insufficient data are available to extend the curve reliably above 120°. An example of the effect is to be found in the spectrum of 1,4-cyclohexadiene, where the mean of the infrared-active and Raman-active frequencies is 1670 cm.$^{-1}$ (infrared, 1658; Raman, 1683). A planar structure for this molecule would lead to C—C=C angles in excess of 120° if the C-C-C angles remain in the neighborhood of 110°.

(10) In the paper of Jones,[3] an alternate structure is proposed for Reppe's solid dimer (structure IV of reference 3). That structure is intermediate between III and IV of Fig. 2, but is inconsistent with the spectra because none of the double bonds in it should have a frequency as high as 1675 cm.$^{-1}$. Jones mentions that this dimer absorbs ultraviolet radiation at wave lengths up to 2500 Å. We have also found this. The implication is that two of the three double bonds are conjugated, but the absorption does not resemble that of 1,3-cyclohexadiene or 1,3-cycloöctadiene.

Experimental

Dimerization of Cycloöctatetraene.—The preparation of cycloöctatetraene dimers was carried out as described by Reppe, *et al.*[2] A portion of the cycloöctatetraene used was prepared by polymerization of acetylene using nickel acetylacetonate catalyst as described by Cope and Estes,[11] and additional cycloöctatetraene was purchased from the General Aniline and Film Company. Through the courtesy of Prof. A. C. Cope, we were also able to investigate a sample of cycloöctatetraene dimer prepared in the laboratories of I. G. Farbenindustrie.

For dimerization of cycloöctatetraene, 25 g. (0.240 mole) was placed in a 50-ml. round-bottom flask attached to a reflux condenser. The flask was heated in an oil-bath at 160° for 24 hours (b.p. of cycloöctatetraene is 142°), at the end of which period all reflux had ceased. The reaction mixture was distilled through a semi-micro column.[12] The results of a representative fractional distillation were:

Fraction	B.p. (uncor.) °C.	Mm.	Weight, g.	$n^{25}D$
I	25–60	30.0	3.70	1.5402
II	115–123	0.4	0.50	1.5908
III	123–126	.4	2.80	1.6004
IV	126–126	.4	3.55	1.6024
V	126–126.5	.4	4.43	1.6042
VI	127–128	.4	3.60	1.6050
Hard yellow residue				

Fraction I (3.7 g.) was yellow in color and contained the unreacted cycloöctatetraene. Fractions II to VI, containing the cycloöctatetraene dimer, were clear and colorless. Infrared spectra taken for fractions II to VI were later compared with the spectra of the pure solid and liquid dimer. These revealed that the fractions were a mixture of the two isomers with the relative amount of the solid dimer increasing in the higher boiling fractions. The relative intensities of the bands at 844 cm.$^{-1}$ (liquid dimer) and at 835 cm.$^{-1}$ (solid dimer) were used to estimate the composition of the mixture. The unfractionated dimer mixture was found to be 77% solid dimer. An infrared spectrum taken of the dimer sample obtained from I. G. Farbenindustrie showed it to be about 70% solid dimer.

Preparation of Solid and Liquid Isomers.—The distilled dimer fraction was dissolved in ether and chilled to Dry Ice temperature, as described by Reppe, *et al.*,[2] to crystallize the solid isomer. On the first attempt this separation required chilling for 24 hours and occasional agitation with a glass stirring rod before crystallization occurred. In subsequent preparations crystallization could be induced immediately after cooling by the introduction of a seed crystal.

The separation was carried out as follows: 5 g. of dimer was placed in a 25-ml. erlenmeyer flask and dissolved in 10 ml. of ether. This was cooled in a Dry Ice–acetone-bath, and after crystallization had occurred the supernatant fluid was pipetted off. An additional 10 ml. of ether was added and the crystallization repeated. After three such procedures the crystals were separated by filtration on a büchner funnel and washed with cold ether; yield 2.2 g. of crystals, m.p. 43° (cor.).

Conversion of Isomers on Heating.—A sample of 25 g. (0.120 mole) of dimer, whose infrared spectrum showed it to be mostly in the solid form, was heated for 36 hours in a distillation pot under a Podbielniak column at a pot temperature of 300–350° with the pressure varying from 1 to 20 mm. No distillation ensued because of difficulty in establishing equilibrium in the column. At the end of this period a sample was withdrawn from the pot for infrared study. The spectrum showed a complete transformation of the solid isomer to the liquid form. The spectrum was identical with that previously obtained for the liquid with the exception of the bands indicative of small amount of solid in the liquid, all of which had vanished in the heat-treated product. Thus, the solid dimer can be quantitatively converted to the liquid simply by heating. The liquid dimer was then distilled through a Holzman column: yield 24.0 g., b.p. 126° (0.6 mm.), m.p. 13–14°, $n^{25}D$ 1.5842.

This conversion was also directly observed in two other cases of distillations with a Holzman column. The transformation was accompanied by a rapid rise in temperature, and in one instance occurred with sufficient violence to break the top of the distillation column. This suggests that the conversion is an exothermic reaction. The conversion was also carried out by heating under nitrogen. Ten grams (0.048 mole) of solid dimer was placed in a three-neck flask fitted with an inlet for nitrogen gas, an outlet and a water-cooled condenser. The flask was heated in an oil-bath for 8 hours and the conversion occurred at 210°. An infrared spectrum was recorded on the product thus obtained, and showed it to be liquid dimer, free of the solid; yield quantitative.

Hydrogenation Studies.—Reppe, *et al.*,[2] reported that the solid dimer shows three double bonds per molecule and the liquid two double bonds. This was confirmed. Hydrogenation of the solid was carried out as follows: 0.152 g. of platinum oxide and 5 ml. of glacial acetic acid were placed in an erlenmeyer flask attached to a gas buret. After the system was flushed three times with nitrogen and then with hydrogen, the catalyst was reduced; 0.197 g. (0.00095 mole) of solid dimer was added and the hydrogenation carried out. After two hours the compound absorbed 66.5 ml. of hydrogen (S.T.P.), 103% of the amount of hydrogen calculated for three double bonds. The reaction mixture was filtered to remove the catalyst and the acetic acid neutralized with concentrated sodium hydroxide. After neutralization, the solution was extracted with ether. The ether solution was dried over magnesium sulfate and filtered with a büchner funnel to remove the drying agent. The ether was then taken off at atmospheric pressure through a Holzman column and the product distilled; yield 0.15 g., b.p. 101° (0.1 mm.), $n^{25}D$ 1.5643.

The hydrogenation of the liquid dimer by Reppe, *et al.*,[2] made use of the palladium-on-charcoal as a catalyst. In the present work a platinum catalyst was employed. The compound took up 102% of the amount of hydrogen calculated for two double bonds with a constant rate. The infrared spectrum of the compound thus obtained showed no frequencies in the double bond region. As before, the catalyst was removed by filtration, the acetic acid neutralized and the hydrocarbon was then distilled; yield 3.6 g., b.p. 116° (0.4 mm.). Recrystallization from absolute ethanol yielded white crystals, m.p. 34–36° cor. (lit.[2] 33–35°).

An interesting feature of the dimers is the fact that the liquid dimer yields a solid product on hydrogenation, whereas the solid dimer yields a liquid.

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