

Structures have been assigned to two new compounds resulting from a series of reactions, starting with one of the di-addition products.

The reaction of 2-methyl-1,4-naphthoquinone

with phenyllithium gave no solid products.

The three products tested showed no Vitamin K activity.

POUGHKEEPSIE, N. Y.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

The Ultraviolet Absorption Spectrum of 1,3-Cyclopentadiene*

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The absorption spectrum of 1,3-cyclopentadiene was measured as a part of an extensive spectroscopic study¹ of unsaturated hydrocarbons which has been in progress in this Laboratory for several years. This compound was of particular interest from two points of view: first, because measurements of the intense absorption band at 43,000 cm^{-1} could be made both of the vapor and of the solution in hexane under comparable conditions and thus afford a basis of study of the oscillator strength of this band and the effect of the solvent; and, second, because the far ultraviolet absorption beginning at 50,000 cm^{-1} consists of a group of sharply defined bands whose vibrational structure could be analyzed.

The absorption of cyclopentadiene and its dimer was measured by Stobbe and Dünnhaupt² between 23,000 and 27,000 cm^{-1} in the course of a study of the polymerization. A study of the spectrum at higher frequencies has been made by Scheibe and Grieneisen³ and will be referred to later.

Experimental

Preparation of Cyclopentadiene.—The cyclopentadiene was prepared by repeatedly cracking and repolymerizing crude dicyclopentadiene using the method followed by Kistiakowsky and co-workers.⁴ The technical dicyclopentadiene⁵ was distilled once and then cracked by passing through a nitrogen filled 120-cm. column packed with glass beads and maintained at a temperature of 40–45°. The cyclopentadiene so obtained was purified by distillation in a long Crismer column and a product boiling between 39.4 and 40.2° was obtained. This was refluxed in air for ten hours on a steam-bath to form white crystals of the dimer

which were then distilled twice at reduced pressure to purify them further. The pure dicyclopentadiene was cracked in a Fenske column in the absence of oxygen and the resulting cyclopentadiene, b. p. 40.2°, used immediately for the spectral measurements. A second series of measurements were made on material which had been subjected to further polymerization and cracking with agreeing results. Difficulty was experienced in determining the refractive index and density because of the polymerization of this compound when it is exposed to air. The lowest values recorded were n_D^{20} 1.4437 and d_4^{20} 0.8073.

Measurement of Absorption.—The absorption spectrum from 32,000 to 46,000 cm^{-1} was photographed with a Hilger quartz prism spectrograph. Both the vapor and the solution were measured by the Henri method of comparisons using a copper-silver spark. The vapor was photographed in a 5-cm. quartz tube at measured pressures ranging from 0.01 to 80 mm. and its spectrum compared with that of the evacuated tube. The solutions in optically pure hexane were measured in matched Baly tubes. Photographs of both vapor and solution were taken using a hydrogen discharge tube as light source and ultraviolet sensitized plates in order to determine the positions of the narrow bands. The latter were measured both directly and from microphotometer records.

The vapor spectrum from 44,000 to 66,000 cm^{-1} was measured with a Hilger fluorite prism vacuum spectrograph using flowing vapor to minimize photodecomposition.⁶ The spectra were recorded on Ilford Q plates and microphotometer records made.

Discussion of-Results

The absorption curves of cyclopentadiene and dicyclopentadiene as measured with the quartz spectrograph are shown in Fig. 1, where the logarithm of the molecular extinction coefficient is plotted against the wave number. The curve of the cyclopentadiene vapor consists of an intense band with maximum about 43,000 cm^{-1} on which is superimposed a number of narrow bands while that of the solution of cyclopentadiene in optically pure hexane is of about the same intensity but is shifted toward the visible by about

* Presented before the Division of Physical and Inorganic Chemistry at the Detroit meeting of the American Chemical Society, September, 1940.

(1) Carr and Stücklen, *J. Chem. Phys.*, **4**, 760 (1936); **6**, 55 (1938).

(2) H. Stobbe and F. Dünnhaupt, *Ber.*, **52**, 1436 (1919); "I. C. T.," Vol. V, p. 363.

(3) Scheibe and Grieneisen, *Z. physik. Chem.*, **B25**, 52 (1934).

(4) Kistiakowsky, Ruhoff, Smith and Vaughan, *THIS JOURNAL*, **58**, 146 (1936).

(5) Dicyclopentadiene was obtained from the Duisberg-Niederick Co. in Germany.

(6) For details of technique, see Carr and Stücklen, *J. Chem. Phys.*, **4**, 760 (1936).

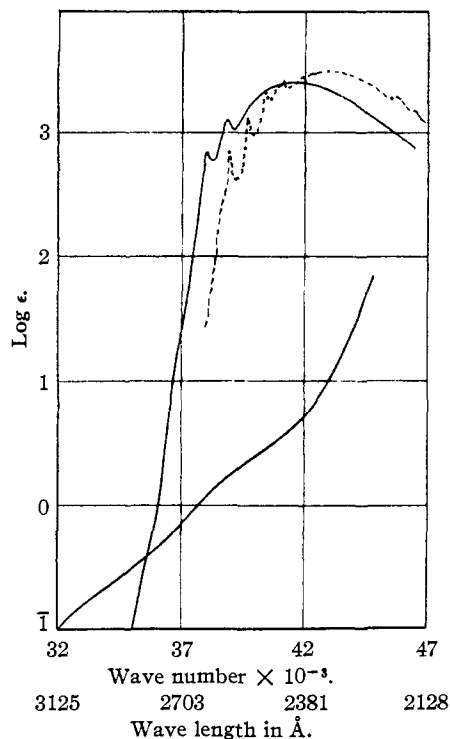


Fig. 1.—Absorption curves of cyclo and dicyclopentadiene in quartz region. Cyclopentadiene: vapor -----; solution —; dimer (lower curve).

1000 cm^{-1} and has but two discernible narrow bands. The positions of the observed maxima in the vapor spectrum are arranged in Table I to show the sequence of stronger bands with separations of nearly 800 cm^{-1} and the weaker, poorly defined bands whose separations are less certain.

TABLE I

WAVE NUMBERS OF DIFFUSE BANDS (IN CM^{-1})		
Stronger bands	Separations	Weak bands
38880		40770
39650	770	41550
40400	750	42240
41170	770	42650
41940	770	43180
45800		
46570	770	46880
47230	660	47940
47940	710	48320
48300		49700

The presence of such an intense absorption band with characteristic narrow bands superimposed makes it possible to identify cyclopentadiene even in minute traces and to estimate its concentration in mixtures of other hydrocarbons. There is an absorption band of comparable intensity for 1,3-cyclohexadiene whose maximum

is however appreciably displaced toward longer wave lengths⁷ and whose structure is different. The aliphatic conjugated dienes of five and six carbon atoms have been found⁸ to have absorption of low intensity in this region and to have the first strong absorption band at frequencies higher by 4000 cm^{-1} . No other type of aliphatic hydrocarbon yet studied has shown this characteristic intense absorption, and the aromatic hydrocarbons have spectra which are readily distinguishable by their structure.

The absorption curve of dicyclopentadiene in hexane solution is also shown in Fig. 1. Its absorption is much less intense than that of the monomer and there is no evidence of narrow absorption bands. The curve has the same general appearance as those of the olefinic hydrocarbons containing two isolated double bonds and substantiates the generally accepted formula for dicyclopentadiene. Attempts were made to measure the spectrum of the vapor but the absorption is so slight at the maximum vapor pressure obtainable at moderate temperatures that no results of significance were obtained.

It is possible that there is some polymerization during the spectral measurements of the monomer and the effect of this had thus to be considered. It is obvious that dimerization would lower the absorption curve of the monomer but since the absorption is measured on a logarithmic scale, even as much as 10% polymerization would lower the curve only 0.04 unit.

The oscillator strength or effective number of dispersion electrons may be estimated from the area under the absorption curve by the formula

$$f = 4.2 \times 10^{-8} \int k d\nu$$

where $k = 2.3\epsilon/24$ at room temperatures and the integral is measured by the area under the curve where k is plotted against wave number. In this way, Mulliken⁹ has found f values for many dienes and other organic compounds and has compared them with values calculated from theoretical considerations. Since comparatively few measurements of vapor spectra have been available, f values have been calculated from absorption curves of solutions and have been corrected for Lorentz-Lorenz forces by a factor $9n/(n^2 + 2)^2$

(7) Henri and Pickett, *J. Chem. Phys.*, **7**, 439 (1939).

(8) Carr and Stücklen, "Proceedings of Seventh Summer Conference in Spectroscopy M. I. T.," John Wiley and Sons, New York, N. Y., 1940, p. 128; unpublished work.

(9) Mulliken, *J. Chem. Phys.*, **7**, 14, 339 (1939); private communication.

where n is the refractive index of the solvent at the wave length of the band maximum. Mulliken has noted that the f value calculated for cyclopentadiene on the basis of earlier data, 0.04 to 0.05, is lower than the predicted value and has offered a partial explanation of this fact. The present data yield a value of approximately 0.07 which is in better agreement with the quantum mechanical calculations.

In order to test the application of the solvent correction a comparison of the areas under the absorption curves of cyclopentadiene vapor and solution have been made in this study. In spite of the uncertainty inherent in this method it seems most unlikely that the area under the vapor curve is appreciably smaller than that under the solution. This leads to the conclusion, either that the Lorentz-Lorenz correction is not valid or that there is a compensating factor, and that the "uncorrected" values from solution data form a better approximation to the true ones than corrected values. A similar finding was made in the case of cyclohexadiene.⁷

In the Schumann region there is a prominent group of narrow, discrete bands between 50,350 and 54,000 cm^{-1} . These bands appear at slightly higher pressures than those necessary to bring out the absorption band described above so that they are hence somewhat lower in absorption coefficient. At low pressures these bands appear clearly defined but at higher pressures numerous weaker bands appear and all are broadened so that they merge together. Figure 2 is a microphotometer record of a plate taken at fairly low pressures to show the more prominent absorption bands. The positions of the bands which were sufficiently sharp to admit of accurate measurement are listed in Table II. These data were obtained by averaging the measurements of at least three plates with the Hilger comparator and were checked by measurements of microphotometer records, and represent a precision of less than 10 cm^{-1} . Nine of the stronger bands have been recorded by Scheibe and Grieneisen with results which agree well within the 100 cm^{-1} which these authors give as the probable precision of their measurements.

Analysis of these data showed that two band systems with similar structures seemed to be present. The two strongest bands at 50,450 cm^{-1} and 50,900 cm^{-1} represent the O-O transitions. The two bands (d and d') next highest in intensity

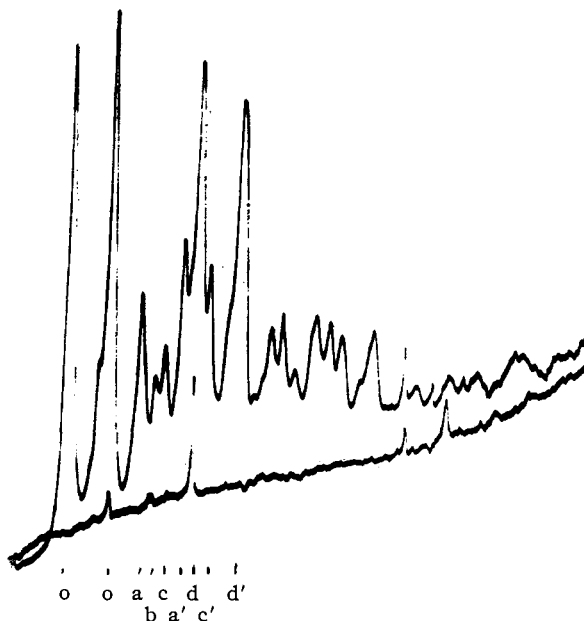


Fig. 2.—Microphotometer record of stronger bands in Schumann region with the light source for comparison.

TABLE II
ABSORPTION BANDS OF CYCLOPENTADIENE

Wave no.	l	Separation	Assignment
50370	vw	-80	
50450	vs	0	O-O
50750	vw	-155	
50830	w	-75	
50905	vs	0	O-O
51220	s	770	<i>a</i>
51380	m	930	<i>b</i>
51500	m	1050	<i>c</i>
51680	s	775	<i>a'</i>
51745	vw	1295	
51860	vs	1410	955 <i>d</i>
51975	s	1070	<i>c'</i>
52170	vw	1265	
52305	m	1855	2 <i>b</i>
52345	vs	1440	<i>d'</i>
52480	vw	2030	
52645	m	2195	<i>a + d</i>
52780	m	1875	2 <i>b</i>
52905	w	2455	<i>b + d</i>
53070	m	2620	
53125	m	2220	<i>a' + d'</i>
53275	m	2825	2 <i>d</i>
53400	m	2495	<i>b' + d'</i>
53600	vw	2695	
53700	w	2795	
53750	m	2845	2 <i>d'</i>

^a There are visible a number of weaker bands at higher frequencies which are not listed because of uncertainties of position. Among these are bands at 54065, 55150, 56050 and 56520 which are thought to represent the third and fourth overtones of the d and d' frequencies.





are separated from these O-O bands by 1410 and 1440 cm.^{-1} , respectively, and hence represent the most prominent vibrational frequencies of the excited molecule. Between these occur bands *a*, *b*, *c* of moderate intensity whose separations identify them as three other vibrational frequencies of band system I of 770, 930 and 1050 cm.^{-1} . Corresponding bands are found for system II; the second however seems to coincide with the intense band of system I mentioned above and is evidenced by an increase in the apparent intensity of the latter, with the result that its position cannot be determined with the accuracy of the other measurements. Nearly all of the other distinct bands may be identified as overtones or combinations of these four vibrational frequencies. There are a few weak bands which cannot be assigned in this way and are thought to be transitions where the change in vibrational quantum number is zero or an even number. Thus those bands of longer wave length than the O-O bands are believed to represent transitions from low lying vibrational levels of the normal molecule to the corresponding vibrational levels of the excited electronic state of the molecule. The bands at 1295 and 1265 cm.^{-1} , respectively, in the two systems may indicate excited vibrational levels of 648 and 633 cm.^{-1} . There are so many possible assignments for the bands of higher frequency in a molecule of as many atoms and low symmetry as cyclopentadiene that these are not shown but it may be said that it is possible to give a reasonable explanation for all bands which are observed.

Thus there seem to be two band systems both of which involve four prominent vibration frequencies which correspond quite closely. These are shown in Table III. The bands of the second system are slightly higher in frequency and in intensity than those of the first.

Cyclopentadiene may be presumed to have C_{2V} symmetry with all of the atoms except the two hydrogens of the methylene group in a plane. Such a molecule would have twenty-seven vibrational frequencies, all of which would be Raman active. Nine of these frequencies would be ring vibrations and of these four would be totally symmetrical if the symmetry assignment is correct. These four totally symmetrical vibrations are the ones most likely to undergo change in an electronic transition. It therefore seems evident that the four prominent vibration frequencies are totally symmetrical vibrations.

The Raman spectrum of this molecule has been studied by several observers¹⁰; one of these, Reitz,¹¹ has made measurements with polarized light and has from the depolarization factors identified the four totally symmetrical vibrations of the ground state of the molecule. The values which he gives for these are shown in Table III and it can be seen that they show a correspondence with the vibrations of the excited state determined in this study. The change in vibrational frequency from the ground to the excited state is less than ten per cent. except in the case of the lowest frequency where a greater change is to be noted. The corresponding normal vibrations are pictured as given by Reitz.

TABLE III
TOTALLY SYMMETRICAL RING VIBRATIONS OF CYCLOPENTADIENE

Band system	Vibration frequencies in cm.^{-1}			
50450	770	930	1050	1410
50905	775	960?	1070	1440
Ground state	911	990	1105	1496
Vibrations				

The results of this study provide an interesting comparison with similar studies of furan.¹² Furan has very low absorption at frequencies below 44,000 cm.^{-1} while cyclopentadiene has very intense absorption in this region. Furan has one system of sharp bands beginning at 52,230 cm.^{-1} while cyclopentadiene has two band systems at 50,450 cm.^{-1} . However, the vibrational structures of the band systems for the two molecules are strikingly similar and show vibrational frequencies of nearly the same magnitude. Furan and cyclopentadiene are ordinarily written with similar structural formulas differing only in the replacement of an oxygen atom with a methylene group. Thus the symmetry of the two molecules and the distribution of mass are very similar and lead to the expectation of similar vibrational frequencies. The chemical behavior of the two molecules shows greater contrast than the substitution would demand. Cyclopentadiene undergoes rapid polymerization and addition reactions while furan is aromatic in nature and has greater stability. The resonance energy of furan is given by Pauling¹³ as 23 kcal. per mole and that of

(10) Kohlrausch, "Der Smekal-Raman-Effekt," J. Springer, Berlin, 1938, p. 158.

(11) Reitz, *Z. physik. Chem.*, **B38**, 386 (1938); **B35**, 374 (1937).

(12) Pickett, *J. Chem. Phys.*, **8**, 293 (1940).

(13) Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1939, pp. 130, 202.

cyclopentadiene is much lower. Hence it is both reasonable and significant that the electronic transitions in the two molecules should be so different in energy and probability of occurrence.

We wish to thank Drs. Emma P. Carr, Mary L. Sherrill and Hildegard Stücklen for their interest and assistance.

Summary

The ultraviolet absorption spectrum of 1,3-cyclopentadiene vapor between 32,000 and 66,000 cm^{-1} consists of a broad intense band with maximum at 43,000 cm^{-1} on which are superimposed

narrow diffuse bands, and a group of sharply defined narrow bands beginning at 50,000 cm^{-1} . Conclusions have been drawn regarding the oscillator strength of the broad band. Analysis of the vibrational structure of the discrete bands reveals at least two band systems with four prominent vibrational frequencies comparable to the totally symmetrical frequencies observed in the normal molecule.

The absorption spectra of solutions of cyclopentadiene and its dimer have also been measured.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Solid Free Radical as Catalyst for Ortho-Para Hydrogen Conversion^{1a}

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Low temperature conversion of ortho-para hydrogen can be brought about by active charcoal, active metals and paramagnetic metallic oxides.² The catalytic effect of the above substances is ascribed in general to the effect of the inhomogeneous magnetic field of the paramagnetic catalyst on the physically adsorbed hydrogen. The theory of the magnetic conversion has been given by Wigner³ and Kalckar and Teller.⁴

The object of the present investigation was to determine whether the list of solid substances catalytically active for this transformation could be extended to include solid free radicals. The latter due to their free unsaturated valence should give rise according to quantum theory to a paramagnetism of a definite magnitude. The organic free radical chosen for this investigation was α, α -diphenyl- β -picrylhydrazyl. This divalent nitrogen radical is rather easy to prepare, is highly dissociated in the solid state and is stable in air. The investigation consisted in the measurement of the magnetic susceptibility of the solid free radical to determine the extent of dissociation and in the measurement at liquid air temperatures of the hydrogen adsorption and the ortho-

para hydrogen conversion rate on the free radical, zinc oxide and an intimate mixture of the free radical and the zinc oxide.

Materials

Zinc oxide was prepared by heating zinc oxalate in a muffle furnace at 400° until all visible decomposition ceased and then continuing the heating for ten hours at 450°.⁵

N-Nitroso-diphenylamine was prepared from diphenylamine according to the directions of E. Fischer.⁶

N,N-Diphenylhydrazine was prepared by reduction with zinc and acetic acid of the N-nitrosodiphenylamine.⁶

α, α -Diphenyl- β -picrylhydrazine was prepared from N,N-diphenylhydrazine and picryl chloride. It was recrystallized from ethyl acetate and had a melting point with decomposition of 172-173°.⁷

α, α -Diphenyl- β -picrylhydrazyl was prepared from the corresponding hydrazine by oxidation in chloroform solution with lead dioxide. It was recrystallized from hot chloroform and absolute ether.⁷

Hydrogen was tank hydrogen which was purified by passage over platinized asbestos at 300° and dried by calcium chloride, ascarite and phosphorus pentoxide.

1,1-ortho-para hydrogen was made by passing the above purified tank hydrogen over chromium oxide gel at liquid air temperature.

Zinc oxide-free radical mixture was made by grinding in a mortar equal weights of the two constituents.

Procedure

The magnetic susceptibilities were determined by the method of Gouy using the apparatus described by Selwood.⁸ The measurements were carried out with mag-

(1a) Presented at the St. Petersburg, Florida, meeting of the American Chemical Society in the spring, 1934.

(1b) Present address, Northwestern University, Evanston, Ill.

(2) Schwab, Taylor and Spence, "Catalysis," D. Van Nostrand Co., New York, N. Y., p. 213; Farkas and Farkas, "Light and Heavy Hydrogen," Cambridge Press, Cambridge, 1935, p. 89.

(3) Wigner, *Z. physik. Chem.*, **B23**, 28 (1938).

(4) Kalckar and Teller, *Proc. Roy. Soc. (London)*, **A150**, 520 (1935).

(5) H. S. Taylor and D. V. Sickman, *THIS JOURNAL*, **54**, 602 (1932).

(6) Fischer, *Ann.*, **190**, 174 (1878).

(7) Goldschmidt, *Ber.*, **55**, 628 (1922).

(8) P. W. Selwood, *THIS JOURNAL*, **55**, 3161 (1933).