Estimates of N_s are given in Table IV; unfortunately, not too great reliability can be accorded these estimates because of the uncertainty in the data at the highest and lowest vapor pressure regions. The BET and Langmuir values for the 48 and 72% substituted materials agree roughly so that we can probably believe that the order of magnitude is correct. The N_s data as obtained from the modified Raoult's law are least reliable; they suggest that the polymers change their structure as they swell in such a direction as to make all of the OH groups accessible for water sorption. At the present time we shall accept this suggestion as being the correct explanation for the anomalous behavior of the polyvinylmethoxyacetals in sorbing water.

Acknowledgments.—This work is part of a general program of study of the thermodynamics of high polymers, for which grants have been gratefully received from Visking Corporation, the Rayon Technical Division of E. I. du Pont de Nemours and Company, the Richardson Company and the Research Corporation (Frederick Gardner Cottrell Grant). We are particularly indebted to Dr. C. E. Black III of the Rayon Technical Division of E. I. du Pont de Nemours and Company and Dr. C. J. B. Thor of the Visking Corporation for helpful coöperation and advice.

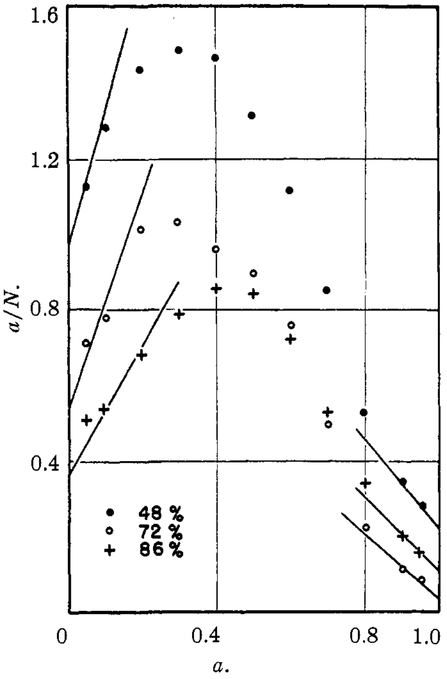

Fig. 4.—Langmuir and modified Raoult's law plot of the water sorption data for the polyvinylmethoxyacetals.

Summary

Water sorption data at 25° are given for eleven synthetic linear polymers, 0/0/100 polyhexamethylene sebacamide, 0/100/0 N-isobutylated polyhexamethylene sebacamide, 100/0/0 N,N'-isobutylated polyhexamethylene sebacamide, 50/0/50 polyhexamethylene sebacamide, N,N'-isobutylated polyhexamethylene sebacamide copolymer, 48, 72 and 86% substituted polyvinylmethoxyacetal, polyhexamethylene adipate and sebacate, polyethylene terephthalate and polyvinylpyrrolidone. The data are interpreted in the light of the BET and other sorption theories. Sorption by the polyesters is so small that it probably occurs only on end-groups. Sorption by polyvinylpyrrolidone is so great that probably every peptide bond serves as a sorption site. Sorption by the polyamides is small and greatly affected by the extent of disorder in the solid. The polyvinylmethoxyacetals sorb water to a much larger extent than expected at high vapor pressures of the water, thus leading us to suggest that more sorption sites become available at higher relative humidities.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 1, 1949

[CONTRIBUTION FROM THE GIBBS CHEMICAL LABORATORY, HARVARD UNIVERSITY]

On the Nature of Thermochromism

BY W. T. GRUBB[*] AND G. B. KISTIAKOWSKY[†]

A number of organic compounds undergo color changes with temperature which are so noticeable that a special name, thermochromism, has been given to the phenomenon. The compounds showing it are some of the substituted ethylenes, with multiple or fused aromatic rings as substituents. Padova[1] proposed that an association–dissociation equilibrium was responsible for the phenomenon and attempted to prove it by molecular weight measurements. Bergmann and Corte[2] demonstrated that Padova's experiments were in error and Bergmann and Engel[3] and others suggested that the formation of diradicals by a partial dissociation of the ethylenic double bond was the cause of thermochromism and supported this proposal by studies of the chemical behavior of such compounds. Probably still stronger chemical evidence was adduced by Schoenberg[4] as support for the existence of an equilibrium between normal ethylenes and betaine-like structures, with

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[*] Harvard University Ph.D. 1949.

[†] Harvard University Faculty 1930–.

(1) Padova, *Ann. Chim. Phys.*, **19**, 386 (1910).

(2) Bergmann and Corte, *Ber.*, **66**, 41 (1933).

(3) Engel, *Z. physik. Chem.*, **B8**, 135 (1930).

(4) Schoenberg, *J. Chem. Soc.*, 442 (1946).

the π electrons of ethylenic linkage shifted to the locus of maximum electron affinity in the molecule. Although much effort has been devoted to the exploration of the chemical behavior of thermochromic compounds, their spectroscopic study appears to have been limited to visual observations and it seemed probable that further light on the origin of thermochromism may be cast by a quantitative study of these spectra. Color changes have been observed in fusion of organic compounds and also on heating homogeneous solutions. Only the latter type of thermochromism will be discussed in the following.

Experimental Details

In planning this investigation it was anticipated that accurate temperature control of long absorption cells may be required, for which the small cell compartment of the Beckman spectrophotometer is not adaptable without major changes in the instrument. Because of this a spectrophotometer was built utilizing as optical parts a "Spekker" photometer and a small Zeiss spectrograph with a quartz Cornu prism for the ultraviolet and a glass prism for the visible part of the spectrum. The plate holder of the spectrograph was replaced by a precision screw-driven slide with a slit, behind which was mounted a RCA 1P28 photomultiplier tube. On the "Spekker" photometer were mounted the thermostat containing the solution and the comparison (solvent) absorption cells, as well as a sector interrupter admitting into the spectrograph alternately the solution and the solvent light beams and so producing through the photomultiplier tube a square wave signal of 30-cycle frequency. The signal was put through one stage of amplification utilizing a 6J5 tube and was rectified by a pair of "Millisec" relays[5] operated by a commutator mounted on the shaft of the sector interrupter. The two direct voltages, each produced by one of the light beams, after amplification by a pair of Horton[6] amplifiers, were applied to the grids of two thyratrons controlling the direction of motion of a reversing motor connected to the extinction drum of the "Spekker" photometer. The effect of this circuit was an automatic equilization of intensities of the two beams.[7] This took a few seconds for completion. The setting of the extinction drum was then read, the photomultiplier tube moved to a different position on the spectrum and the procedure repeated. Aside from some unessential difficulties with the optical system arising from the design of the "Spekker" photometer, which is built for photographic recording, the photometer proved to be entirely satisfactory. A comparison with the Beckman instrument, using azobenzene as a test substance, demonstrated that the extinction coefficients could be determined with about the same reproducibility as with the commercial instrument. Unfortunately, however, the light sensitivity of photomultiplier tubes becomes unacceptably low above 6000 Å. The measurements in the red part of the spectrum had to be made with the Beckman instrument, absorption cells being mounted in a small copper block, electrically heated to the desired temperature. The accuracy of temperature control in these experiments was not better than ±5°, but in view of the insensitivity of spectral changes to temperature, which was established in the course of this work, no serious errors resulted therefrom.

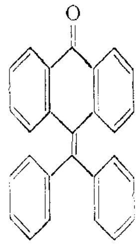
In the experiments with the Spekker-Zeiss combination the absorption cells were mounted in a metal block thermostat whose temperature was controlled to ±1°, or they were put into cavities in another metal block which was cooled by Dry Ice. In these latter experiments a stream of precooled, dry air was sweeping by the windows of the absorption cells to eliminate fogging.

The absorption cells were of fused quartz, with optically polished windows and with short side tubes for filling. One set had an internal length of 1.2 cm., the other of 10.0 cm. A tungsten filament incandescent lamp served as the light source for all experiments.

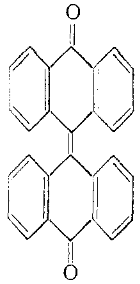
The width of the slit in front of the photomultiplier tube was changed with the spectral region to provide adequate light intensity for the cell and varied from 50 Å. at 3000 Å. to 100 Å. at 5000 Å. The slide carrying the slit and the photomultiplier was geared to a revolution counter. The relation between the readings of the latter and the mean wave length entering the slit was determined with the aid of mercury vapor arc lines.

Spectroscopic observations were made on four compounds for which the literature suggests striking thermochromic properties in solution.

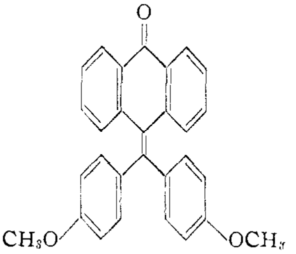
Diphenylmethyleneanthrone was given to us by Dr. Paul E. Fanta. Its m. p. was 205–207°; analysis gave 90.5% C, 5.03% H instead of 90.3 and 4.80 calculated.



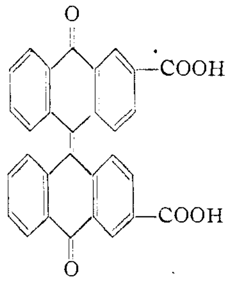
Bianthrone was given to us by Dr. Mayer B. Goren; m. p. 315–320°; analysis 87.5% C, 4.17% H; calculated 88.1 and 4.12, respectively.



Dianisylmethyleneanthrone was synthesized for us by Dr. Carl Moser; m. p. 191–192°; analysis 83.4% C and 5.26% H; calculated 83.3 and 5.15.



Bianthrone 2,2′-dicarboxylic acid was given to us by Dr. Mayer B. Goren; m. p. 340°; analysis 75.8% C and 3.77% H; calculated 76.3 and 3.42.



Decalin (Eastman Kodak Co. Practical Grade) after one passage through a 50-cm. tube of silica gel, "through 200 mesh," acetophenone after one distillation, acetone (Reagent Grade) without further purification and water were the solvents. Highly supersaturated solutions had to be used in most of the experiments at room temperature because of limited solubility of the compounds investigated. In comparing absorption spectra at different temperatures corrections were made for thermal expansion

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(5) Stevens Arnold Company, Boston, Massachusetts.

(6) Horton, *J. Franklin Inst.*, **216**, 749 (1933).

(7) See J. B. Wilkie, *Rev. Sci. Instruments*, **16**, 97 (1945), for a similar circuit.

of the solvents, with the aid of the following density–temperature relations: Decalin[8]: $d = 0.875 - 6.7 \times 10^{-4}(t - 21.5) - 2.1 \times 10^{-6}(t - 21.5)^2$. Acetophenone[9]: $d = 1.026 - 8.5 \times 10^{-4}(t - 21.6) - 6.0 \times 10^{-7}(t - 21.6)^2$. Acetone[10]: $d = 0.812 - 1.11 \times 10^{-3}t - 3.1 \times 10^{-7}t^2$.

The solutions were prepared by pipetting the desired volume of the solvent into a flask containing the weighed amount of the solute and heating the mixture in darkness until complete solution. Light and heat caused slow decomposition of these solutions and fresh samples were used for each absorption curve determination. However, on rerunning at room temperature the absorption curve of a solution that was measured at about 150° showed that its spectrum was changed barely noticeably.

Results and Interpretation

Visual observations of the color changes of these solutions with temperature confirmed indeed the descriptions in the literature. Diphenylmethyleneanthrone and dianisylmethyleneanthrone changed with rising temperature from yellow to red-orange, dianthrone and dianthrone-2,2′-dicarboxylic acid from yellow through green to blue-green. In Figs. 1 and 2 are plotted the molar extinction coefficients of diphenylmethyleneanthrone and of dianisylmethyleneanthrone at one temperature. The same figures contain also plots of the differences between extinction coefficients at several temperatures, enlarged a hundred-fold. The molar extinction coefficients were found to be independent of concentration of the absorbing solute (in the concentration range studied, below about 0.3 g. per liter). This rules out dissociation and association processes as the cause of thermochromism. The difference plots of Figs. 1 and 2 bring out the important characteristics of the temperature effect on these absorption bands: in both compounds a rise in temperature causes a decrease in the extinction coefficients near the center of the band and an increase in the wings. With diphenylmethyleneanthrone a completely symmetrical pattern is obtained. The shape of the curve of its extinction coefficients at room temperature clearly indicates a single absorption band with a maximum near 3550 Å. The dianisylmethyleneanthrone pattern is more complex, but the curve of extinction coefficients at −35°, which has a shoulder near 3400 Å., leaves no doubt that it is the result of superposition of two bands, the stronger one with a maximum at 3780 Å. and a weaker one with a maximum in the region near 3400 Å. If the pattern of temperature effects on each is the same as that observed for diphenylmethyleneanthrone, the superposition must result in the difference plot shown in Fig. 2.

Dianthrone has a strong absorption in the ultraviolet and only the wing of it was quantitatively investigated in the blue-violet region. This region showed a slight decrease in extinction coefficients with rising temperature.

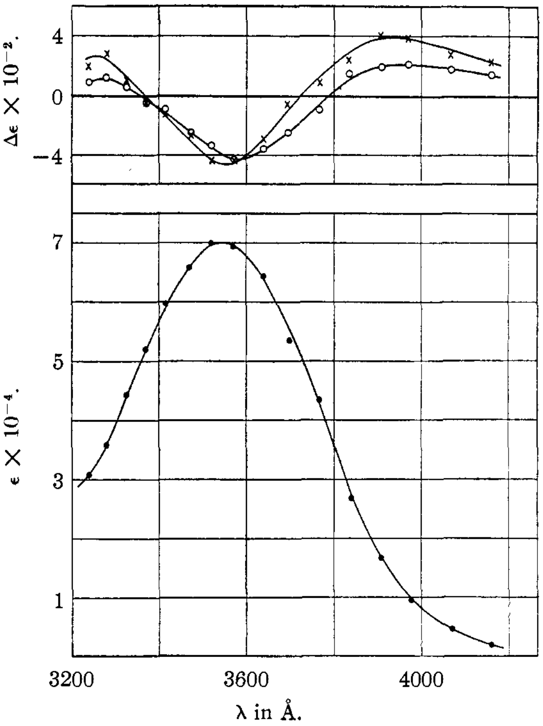

Fig. 1.—Diphenylmethyleneanthrone in decalin: ●, ϵ (molar extinction coefficient) $\times 10^{-4}$ at 28°; O, $(\epsilon_{117°} - \epsilon_{28°}) \times 10^{-2}$; X, $(\epsilon_{153°} - \epsilon_{28°}) \times 10^{-2}$.

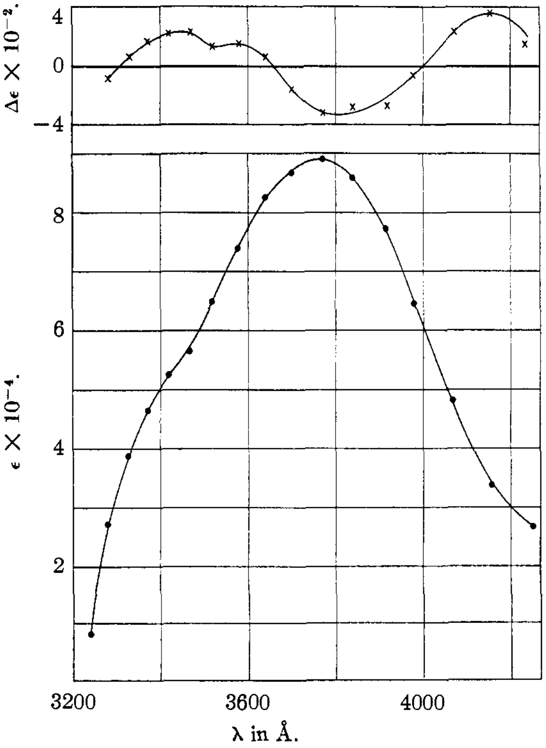

Fig. 2.—Dianisylmethyleneanthrone in acetone: ●, ϵ (molar extinction coefficient) $\times 10^{-4}$ at −35°; X, $(\epsilon_{25°} - \epsilon_{-35°}) \times 10^{-2}$.

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(8) Deduced from data of Doldi, *Ann. Chim. Applic.*, **28**, 454 (1938).

(9) "International Critical Tables."

(10) "International Critical Tables."

Within the accuracy of these measurements, the areas under the extinction curves of the first two compounds do not change with temperature and neither do the wave lengths of the absorption maxima. This finding means that the total number of light absorbing molecules responsible for the absorption bands is independent of temperature. Consequently, a temperature-dependent chemical equilibrium, be it with diradicals or with betaines, cannot be responsible for the observed effects.

Actually it is not necessary to postulate any chemical equilibria to account for the observed changes of absorption bands with temperature, since a straightforward application of the Franck–Condon[11] principle provides a complete if not a quantitative answer. Considering the spectral width of the bands involved, it is evident that they are not single vibrational transitions. They are superpositions of probably numerous vibrational bands all belonging to the same electronic transition, smeared into a continuous band either by the action of the fields of neighboring molecules or by the inadequate resolving power of our instrument. These vibrational transitions probably involve changes in the quantum numbers of several normal vibrations. At low temperatures the vibrational quantum numbers of the absorbing molecules will be preponderantly zero, and therefore, by the Franck–Condon principle, if the equilibrium configurations of the molecules in the upper and the lower electronic states are not too different, the changes in vibrational energy will not be large, regardless of which normal vibration is involved in a given transition. In other words, the frequencies of individual vibrational bands will bunch close to the frequency of the pure electronic transition. Now, as the temperature rises, the light absorbing molecules are raised into higher vibrational quantum states, in accord with the Boltzmann distribution law. The most probable transitions for these molecules involve, by the Franck–Condon principle, different changes of vibrational quantum numbers from those of molecules in the lowest level. The superposition of all these transitions must result in a broadening and flattening out of the over-all absorption curve. No significant changes in the area under the curve should be observable if the smearing out is the effect of neighboring molecules rather than of the inadequate resolving power of the instrument.

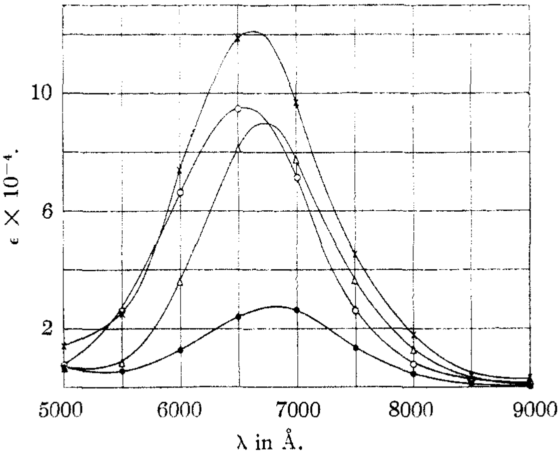

Fig. 3.—Dianthrone: ϵ (molar extinction coefficient) $\times 10^{-4}$ in acetophenone at: ●, 25°; △, 99°; ×, 145°; O, in decalin at 145°.

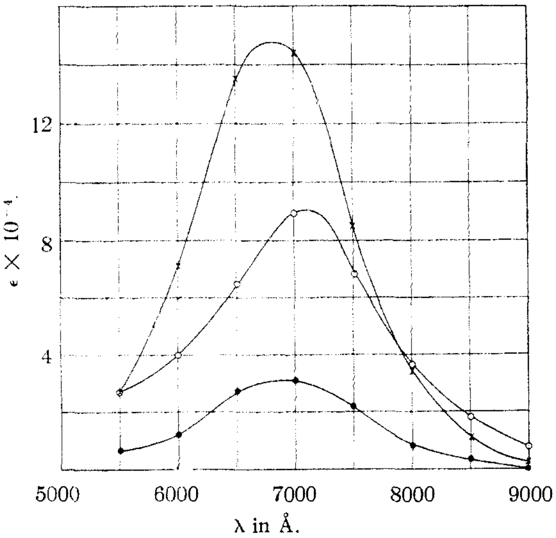

Fig. 4.—Dianthrone-2,2′-dicarboxylic acid: ϵ (molar extinction coefficient) $\times 10^{-4}$ in acetophenone at 25°, ●, and at 145°, ×; in aqueous sodium bicarbonate at 95°, O.

These are precisely the observations made, and we conclude that the thermochromic properties of these two compounds are not directly related to their special chemical properties. The cause of thermochromism here is the possession of an electronic transition near the edge of the visible spectrum and such relative configurations of the normal and the excited states of the molecules that changes in temperature cause large shifts in the frequencies of probable vibrational transitions by the well known mechanism discussed above.

It is probable that visually observed thermochromic properties of some other compounds as well are due to this rather trivial cause, the effect of temperature upon the distribution of molecules among vibrational quantum states.

A more essential cause of thermochromism has been established for dianthrone and the dianthrone-2,2′-dicarboxylic acid through the finding of an additional band in the visible part of the spectrum whose integrated intensity changes with temperature. Figures 3 and 4 show the results at three temperatures and in two solvents for each compound. The extinction co-

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[11] Sponer, "Molekülspektren," Springer, 1936; Lewis and Calvin, *Chem. Revs.*, **25**, 274 (1939).

efficients were found to obey Beer's law and so the dissociation–association equilibria are not responsible for this band. The obedience to Beer's law is also a reasonable guaranty that the continuous appearance of the band is not due to the limited resolving power of the Beckman spectrophotometer. Hence the number of absorbing molecules changes with temperature. An application of the Boltzmann law to the temperature coefficient of the area under the band gives them the energy difference between molecules which do and which do not absorb radiation in this spectral region.

Table I shows the results of these calculations. In carrying them out only the area from the absorption maximum toward the red was used because on the violet side the band overlaps to a slight extent the tail of the ultraviolet absorption region and accurate determinations of the area are not possible.

TABLE I

Compound	Solvent	Temp. range, °C.	ΔH, kcal.
Dianthrone	Acetophenone	25–145	3.1
Dianthrone	Acetophenone	25–99	3.9
Dianthrone	Decalin	22–145	3.3
Dianthrone-dicarboxylic acid	Acetophenone	25–145	3.1
	Aq. sodium bicarbonate	25–99	4.5

The data of Table I show the light absorbing state of these compounds to have 3.5 kcal. higher energy content. Within the experimental accuracy this energy difference is identical for the two compounds and is independent of the nature of the solvent. The area under the absorption curve at a given temperature is also identical for the two compounds in acetophenone as the solvent. In decalin and in water the areas are smaller by about 20%. The absorption maximum is shifted in aqueous solution to the red by about 800 cm.$^{-1}$, a rather common effect.

The width of this absorption band shows it to be a superposition of several vibrational transitions, the upper state evidently being a distinct electronic state. The present measurements reveal, therefore, four states for the two homologous compounds: the normal state (state 1) from which optical transitions, giving rise to the ultraviolet absorption region, take place to a level at about 26000 cm.$^{-1}$ (state 4); state 2, about 1200 cm.$^{-1}$ above the ground level, to which molecules are raised by thermal excitation and state 3, 16000 cm.$^{-1}$ above the ground level, which combines only with state 2. The transition probability from state 1 to state 3 is of the order of or less than 10^{-4} of the transition probability from 2 to 3.[12] The latter probability is of an order of magnitude which suggests a fully allowed transition. Thus, treating states 1, 2, 3 as degenerate states with statistical weight factors p_1, p_2, p_3; assuming that the population of state 2 is in accord with the Boltzmann distribution law and computing the Einstein transition probability B_{23} from the area under the extinction coefficient of the 6600 Å. band (1.27×10^{19} cm. sec.$^{-1}$ mole^{-1} cc. for dianthrone at 418°K.), treated as monochromatic absorption, the Einstein spontaneous transition probability from state 3 to state 2 (A_{32}) is found to be 8×10^6 p_1/p_3. Thus the lifetime of excited molecules is of the order of 10^{-7} seconds. The fully allowed transitions to state 3 from state 2, together with the absence of such transitions from state 1, make it most improbable that states 1 and 2 belong to the same electronic level and differ only in vibrational quantum numbers. Professor R. B. Woodward suggested to us, however, that state 2 may be the coplanar configuration of the two anthrone ring systems, in which the lowering of the energy content by resonance between the two systems, together with the energy lowering caused by the release of strain of the central double bond almost compensate for the energy of steric hindrance of 4,4′ carbon and hydrogen atoms. Indeed one finds in the literature several studies which show that coplanar aromatic systems have absorption spectra shifted toward the red compared with the spectra of more heavily substituted related compounds in which steric hindrance prevents coplanar configuration.[13] If this interpretation is correct, the sharply differentiated absorption spectra observed presently with the same compound suggest that the normal (out of plane) and the coplanar configurations are separated by a very high potential energy barrier, ensuring very thin population of intermediate states. Also, the studies of the potential barriers caused by steric hindrance in biphenyl compounds[14] indicate that in a nearly planar configuration dianthrone should have very large steric hindrance energy. Therefore, since the "coplanar" configuration is only 3.5 kcal. above the ground state, there should be a high potential barrier between the two.

Experiments were made in which a solution of dianthrone in decalin, after heating to 150°, was forced through a narrow silver tubing immersed in ice and so was cooled to room temperature within less than 0.1 second. The spectrum of this rapidly cooled solution was indistinguishable from that of the unheated solution. This observation, by analogy with kinetic

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[12] A comparison of the temperature dependance of the absorption in the interval 25 to 99° with that in the interval 99 to 145°, gives no indication of a temperature-independent component of absorption even at room temperature. Taking the magnitude of this component, which could be due to molecules in state 1, as less than 5% of the total and noting that at room temperature the mole fraction of molecules in state 2 is about 0.002 according to the Boltzmann factor, we arrive at the estimate given above.

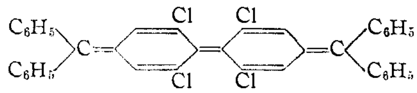
[13] Pickett, Walter and France, THIS JOURNAL, **58**, 2296 (1936); O'Shaughnessy and Rodebush, *ibid.*, **62**, 2906 (1940).

[14] Li and Adams, *ibid.*, **57**, 1565 (1935); Kistiakowsky and Smith, *ibid.*, **58**, 1043 (1936); Westheimer and Mayer, *J. Chem. Phys.*, **14**, 733 (1946).

data on the rates of racemization of biphenyl compounds, shows that the potential barrier must be less than 20 kcal. This low value seems to us to rule out definitely the coplanar configuration of dianthrone as an explanation of state 2.

The betaine structure of dianthrone, having no uncoupled spins, is presumably one of several valence bond structures which must be considered in deriving the real resonance state of the molecule. *A priori*, it is possible that states 1 and 2 are two related resonance states, for instance one even and the other odd. This would account for the observed selection rules, but Professor R. S. Mulliken kindly informed us that in his opinion a separation of only 3.5 kcal. between two such resonance states is highly improbable; with this opinion we are entirely in accord. In view of the participation of betaine structure in the resonance of the molecule, the further existance of a tautomeric betaine structure of different nuclear configuration seems rather improbable. Furthermore, such a non-resonating tautomer would presumably have the properties of a zwitterion and yet the absorption spectrum was found to be virtually independent of the polarity of the solvent.

Mulliken[15] has pointed out that the energy separation of the lowest singlet and triplet levels in ethylenic molecules should decrease with increasing torsion of the double bond. This torsion is present in dianthrone because of steric hindrance between atoms in the 4,4'-positions and we favor, therefore, an interpretation of state 2 (and state 3) as the diradical triplet state of the molecule, with the two halves at approximately 90° angle to each other, whereas the ground state (and state 4) is a singlet, with the double bond in a state of considerable torsion. This interpretation finds strong support in the studies of Mueller and Neuhoff[16] on the magnetic susceptibility of the compound



which was shown to exist partially in paramagnetic state and in some other observations cited by Bergmann.[17]

Summary

The thermochromism of diphenylmethyleneanthrone and dianisylmethyleneanthrone has been shown to be due to a trivial cause, the broadening of a near-ultraviolet absorption region by changing distribution of molecules among vibrational states.

The thermochromism of dianthrone and dianthrone-2,2'-dicarboxylic acid is due to the existance of a distinct electronic level situated 3.5 kcal. above the ground state. By elimination of other possibilities it is concluded that this level is a triplet (diradical) state of the molecules.

CAMBRIDGE 38, MASSACHUSETTS

RECEIVED SEPTEMBER 7, 1949

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[15] Mulliken and Roothaan, *Chem. Revs.*, **41**, 219 (1947).

[16] Mueller and Neuhoff, *Ber.*, **72**, 2063 (1939).

[17] Bergmann, "Isomerism and Isomerisation," Interscience Publishers, Inc., New York, N. Y., 1948.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Isotopic Exchange Reactions of Gaseous Ethyl Bromide with Bromine, Hydrogen Bromide and Deuterium Bromide[1]

BY JOHN B. PERI AND FARRINGTON DANIELS[*]

The thermal decomposition of ethyl bromide into ethylene and hydrogen bromide at elevated temperature has been the object of extended investigations in this Laboratory. Selected in 1932[1a] as a "simple" gas phase reaction it has been used in successive researches[2,3,4] to test prevailing views in the kinetics of gas phase reactions, collision hypotheses, free radicals, chain mechanisms and wall effects.

Following the easiest procedure, commonly accepted in the 1930's, the course of the reaction in most of the experiments was followed by the measurement of total pressure as a function of time, and it was concluded that although the reaction was affected by the glass walls of the vessel and although chain mechanisms could not be ruled out, the main rate-determining step nevertheless was probably the unimolecular breaking of the C–Br bond.

Isotopic tracers have provided a new tool for exploring further into the mechanism of this reaction. Preliminary studies with inadequate amounts of radioactive bromine[5] seemed to show that at temperatures above 325°, bromine in hydrogen bromide exchanged places with the bromine in ethyl bromide, and that the reaction was faster than the decomposition of ethyl bromide, but that at temperatures below 225° only slight

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[*] Harvard University Ph.D. 1914.

[1] More complete details of this investigation may be obtained from the Ph.D. thesis of John B. Peri, filed in the library of the University of Wisconsin in June, 1949.

[1a] E. T. Lessig, *J. Phys. Chem.*, **36**, 2335 (1932).

[2] E. L. Vernon and F. Daniels, THIS JOURNAL, **55**, 922 (1933).

[3] P. Fugassi and F. Daniels, *ibid.*, **60**, 771 (1938).

[4] F. Daniels and P. L. Veltman, *J. Chem. Phys.*, **7**, 756 (1939).

[5] H. M. Hulbert, Ph.D. Thesis, University of Wisconsin, 1942.