hours the rotation was again taken: $[\alpha]^{30}\text{D}$ +77.2 ± 5° ($\alpha^{30}\text{D}$ +1.75 ± 0.1°; l = 2 dm.).

Treatment of 17-Isopregnan-3(α)-ol-20-one with Hydrogen Chloride.—In a manner similar to the above a solution of 44.7 mg. of 17-isopregnan-3(α)-ol-20-one made up to 5 ml. with 4.3% methanolic hydrogen chloride was refluxed for four hours and then the rotation was taken: $[\alpha]^{31}\text{D}$ +75.6 ± 5° ($\alpha^{31}\text{D}$ +1.35 ± 0.1°; l = 2 dm.).

Acetate of 17-Isopregnan-3(α)-ol-20-one.—A solution of 100 mg. of 17-isopregnan-3(α)-ol-20-one in 1 ml. of acetic anhydride and 0.66 ml. of acetic acid was refluxed for twenty minutes. After standing for three hours the solution was diluted to turbidity with water. The acetate separated in fine needles and was collected, weight 95 mg. After one recrystallization from methanol it melted at 157–159° and mixed melting points with both the normal and 17-isopregnanolones gave about 30° depressions: $[\alpha]^{34}\text{D}$ −28.2 ± 8° (24.16 mg. made up to 2 cc. with methanol; l = 1 dm.; $\alpha^{34}\text{D}$ −0.34 ± 0.1°).

Anal. Calcd. for $C_{23}H_{36}O_2$: C, 76.61; H, 10.07. Found: C, 76.82; H, 10.32.

Oxime of 17-Isopregnan-3(α)-ol-20-one.—A solution of 100 mg. of 17-isopregnan-3(α)-ol-20-one, 100 mg. of hydroxylammonium chloride, and 150 mg. of sodium acetate (trihydrate) in 2 ml. of methanol and 0.5 ml. of water was refluxed for two hours. After cooling the solution was poured into water, extracted with ether, and the ether solution was dried over anhydrous sodium sulfate. The ether was removed and the residue was crystallized first from dilute acetone and then from methanol giving a white crystalline oxime melting at 192–197° (with decomposition). A mixed melting point with a sample of the oxime of the normal pregnan-3(α)-ol-20-one[6] gave a depression of about 20°.

Anal. Calcd. for $C_{21}H_{35}O_2N$: N, 4.20. Found: N, 4.57.

Test with Digitonin.—To about 1 mg. of 17-isopregnan-3(α)-ol-20-one in a few drops of 90% methanol was added an equal volume of a saturated solution of digitonin in 90% methanol. No precipitate was obtained even after standing for several hours.

Summary

17-Isopregnan-3(α)-ol-20-one has been isolated from the mother liquor from the crystallization of pregnan-3(α)-ol-20-one prepared by alkaline hydrolysis of its acetate, and the acetate and oxime were prepared.

Refluxing normal or isopregnanolone with either methanolic sodium hydroxide or hydrogen chloride solution produced mixtures of these isomers in approximately the same ratio.

(6) Butenandt and Müller, *Ber.*, **71**, 191 (1938).

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Phosphorescence and the Triplet State

BY GILBERT N. LEWIS AND M. KASHA

1. **Introduction.**—The property of afterglow, or phosphorescence, in spite of its inherent interest and practical importance, has seemed far removed from more commonly studied physical and chemical properties. We propose, however, to show that a spectroscopic study of phosphorescence provides quantitative data concerning an extremely important state of every type of molecule, the triplet state.

Phosphors may be divided into two classes.[1] The first comprises the "mineral phosphors," in which the active centers are regions of physical or chemical inhomogeneity in a crystalline mass. Their activity cannot be ascribed to well-defined molecular species. In phosphors of the other class phosphorescence may be ascribed to a definite substance, whether this substance is in the pure crystalline state, or adsorbed on a foreign surface (including adsorption on the filaments which form the structure of a gel), or finally, dissolved to form a homogeneous transparent solution in a solvent which is usually, through supercooling, in a rigid or glassy state. It is with these homogeneous solutions that the present paper will deal.[2]

As to the cause of phosphorescence, it is supposed in the case of mineral phosphors that light causes the ejection of an electron from some point in the phosphor, and that after a time the electron returns with re-emission of light. This is certainly not the phosphorescent process for an organic substance dissolved in a rigid medium. The ejection of electrons from many such molecules has recently been studied.[3,4,5,6] The energy necessary for electron ejection is higher than that needed for phosphorescence, and the absorption spectrum of the resulting substance is entirely different from that in the phosphorescent state, as illustrated in the case of diphenylamine.[3] Moreover, such a mechanism would be incompatible with the observed[7,8,9,10] strictly exponential decay of an organic phosphor. This first-order rate of decay proves that a single molecule in the phosphorescent state undergoes the process or processes responsible for phosphorescence.

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[1] For the earlier literature concerning phosphors we may refer to P. Pringsheim, "Fluorescenz und Phosphorescenz," 3rd ed., Julius Springer, Berlin, 1928, and P. Lenard, F. Schmidt and R. Tomaschek, "Handbuch der Experimental Physik," **23**, Akad. Verlag., Leipzig, 1928.

[2] Many of the substances whose phosphorescence we have studied in rigid solutions give equally characteristic phosphorescence spectra in the pure crystalline state, either at room temperature, or at the temperature of liquid air, usually with a considerable displacement toward the red. It has seemed best to restrict our attention at present to the more easily interpretable dilute solutions.

[3] Lewis and Lipkin, THIS JOURNAL, **64**, 2801 (1942).

[4] Lewis and Bigeleisen, *ibid.*, **65**, 520 (1943).

[5] Lewis and Bigeleisen, *ibid.*, **65**, 2419 (1943).

[6] Lewis and Bigeleisen, *ibid.*, **65**, 2424 (1943).

[7] R. Tomaschek, *Ann. Physik*, **67**, 612 (1922).

[8] Schischlowski and Wawilow, *Physik. Z. Sowjetunion*, **5**, 379 (1934).

[9] Lewschin and Vinokurov, *ibid.*, **10**, 10 (1936).

[10] Lewis, Lipkin, and Magel, THIS JOURNAL, **63**, 3005 (1941).

2. The Reality of the Phosphorescent State.—The understanding of phosphorescence was more difficult because of the existence of two types of afterglow, of different frequencies, but coming from the same excited molecule, as shown by the identity in the lifetime of the two phosphorescences. Of the two processes by which the molecule returns from the phosphorescent state to the ground state with emission of light, the alpha and beta processes,[10] the first gives an emission spectrum identical with that of fluorescence, and approximates to a mirror image of the absorption spectrum. The beta spectrum, on the other hand, has not hitherto been calculable either as to position or structure.[11] The speed of the alpha process increases rapidly with temperature, while the beta process is nearly independent of temperature and undoubtedly would continue even down to the absolute zero.[10]

The first step in the interpretation of the alpha and beta processes we owe to Jablonski.[12] He assumed a metastable or phosphorescent state lying below the fluorescent state. From this phosphorescent state a molecule could pass directly to the ground state by the beta process, or it could be activated thermally to the energy of the fluorescent state and then return to the ground state by the alpha process. This theory was quantitatively verified by Lewis, Lipkin and Magel[10] and we reproduce in Fig. 1 their Jablonski diagram for fluorescein in boric acid glass, to which we have added our own determination of the energy of the second electronically excited state of fluorescein in an acid medium. The interval S–S″ represents the energy corresponding to the second main absorption band, which happens to be a *y* band. We have also used other letters to designate the several states in conformity with the theory that we are about to develop. The closely spaced lines, indicating the vibrational levels, are purely schematic. Later we shall give data for numerous organic molecules, showing some of the complex vibrational states of the lowest electronic state.

An assumed state becomes real when its properties are measured. Lewis, Lipkin, and Magel[10] were able to show that with increasing illumination the amount of phosphorescence approached a saturation value where as much as 80% of the fluorescein was in the phosphorescent state. It was thus possible to determine the absorption spectrum of the molecules in the phosphorescent state just as though they were ordinary molecules. Two bands were found corresponding to excitation to two levels marked T′ and T″, and the remarkable fact was established that molecules passing from the T to the T′ and T″ states, by absorption of light, returned directly to the T state and not to the S or any other state. We shall see that this observation furnishes a powerful argument for the theory of the phosphorescent state that we are going to propose.

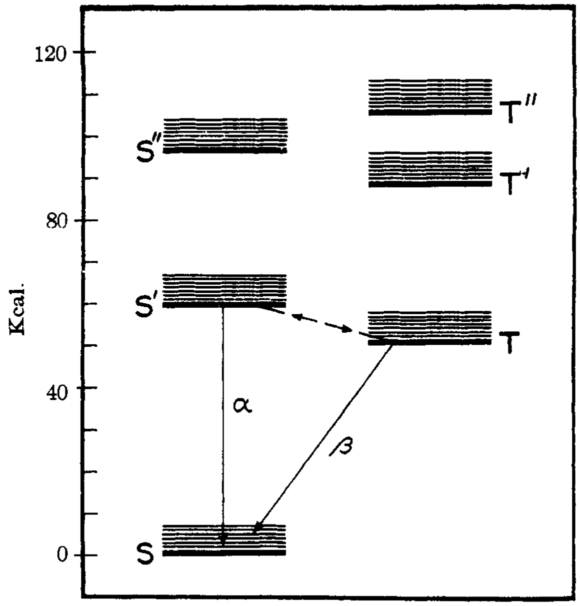

Fig. 1.—Jablonski diagram for fluorescein in boric acid glass (in part after Lewis, Lipkin, and Magel[10]).

Because the alpha process is merely a duplication of fluorescence, and because it usually becomes negligible at the low temperature at which most of our experiments were made, for the remainder of this paper we shall consider beta phosphorescence only.

3. Phosphorescent State Unique.—There is nothing in the previous literature to indicate that a single substance has only one long-lived phosphorescent state. In 1896 Schmidt[13] found that methyl violet, in addition to its red phosphorescence, also has a green phosphorescence. It has since been found[14] that the similar dye, crystal violet, has one phosphorescence in the infra-red and one in the green, both due to beta processes, but stimulated by different frequencies, and having different half-lives. We shall return to this phenomenon presently.

Goldstein,[15] in an extensive series of investigations, studied phosphorescence chiefly in pure crystals excited by cathode rays, but he also used ultraviolet light and solutions in rigid alcohol at low temperatures. In general he found two sets of phosphorescence bands. One, which he called the "Vorspektrum" appeared at the moment of illumination. The second, which he regarded as more characteristic and therefore called the "Hauptspektrum," appeared after

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[11] Under illumination with polarized light the alpha phosphorescence is polarized just as the fluorescence is, but the beta phosphorescence shows very little polarization, sometimes negative as in the case of acridine orange (Pringsheim and Vogels, *Acta Phys. Polon.*, **4**, 341 (1935)), sometimes positive.[10] An ingenious experiment by Weissman and Lipkin (THIS JOURNAL, **64**, 1916 (1942)) has shown that, peculiar as the beta process is, it is an electric dipole emission.

[12] A. Jablonski, *Z. Physik*, **94**, 38 (1935).

[13] Schmidt, *Ann. Physik*, **58**, 103 (1896).

[14] Lewis, Magel, and Lipkin, THIS JOURNAL, **64**, 1774 (1942).

[15] E. Goldstein, *Physik. Z.*, **11**, 430 (1910); **12**, 614 (1911); **13**, 577 (1912).

some illumination. The several investigations in this Laboratory, of photochemical changes in rigid media, indicate that Goldstein's "Hauptspektrum" is indeed a characteristic phosphorescence, not of the original substance, however, but of the substance produced therefrom by simple photo-oxidation, *i. e.*, by the ejection of an electron.

von Kowalski[16] in his many valuable papers on the phosphorescence of organic substances drew especial attention, even in a lecture demonstration, to the short life of the red bands as compared to the life of the green and blue bands of the same substance. If true this would prove the existence of more than one phosphorescent state.

Also in our own first experiments there were many indications of more than one phosphorescent state. Thus with some substances, *e. g.*, α-nitronaphthalene, α-naphthaldehyde, 2-nitrofluorene, and 4,4′-dinitrobiphenyl, changes of color were observed, either with decay of phosphorescence, or with change in character of the exciting light. However, it was found possible to purify these substances to the point where these phenomena disappeared, and all our succeeding experiments show that for every substance there is a unique phosphorescent state.

It is true we have often encountered the Goldstein effect. Thus, anthraquinone was illuminated in the phosphoroscope for five minutes with the light of the high-pressure mercury arc; then the camera was opened for seventeen minutes giving the photograph shown in Plate I, 27; the plate was moved and exposed for thirty minutes more giving 27a; again the plate was moved and exposed for another thirty minutes giving 27b. It is evident that 27 is the spectrum of pure anthraquinone; 27a that of a mixture; 27b chiefly that of the new substance, the original anthraquinone being nearly destroyed. This last spectrum is in all probability the phosphorescence of the positive ion produced by the ejection of an electron from anthraquinone.

It has been shown by Lewis and Bigeleisen[5] that in the photo-oxidation of the base of Wurster's Blue, and of leuco methylene blue, the photochemical reaction is of the first order with respect to the photons. This is doubtless true also of the change occurring in anthraquinone. However, in the course of our present work we have found several instances of a new class of photochemical reactions which are of the *second order with respect to the photons*. When α-nitronaphthalene in EPA (see experimental section), at liquid air temperature, is exposed to intense ultraviolet light and viewed directly without a phosphoroscope, it shows a brilliant yellow luminescence (Plate I, 22), which changes after a few minutes[17] exposure to an equally brilliant pink (Plate I, 22a), which in turn is followed by a blue. Sometimes all three colors appear on the same sample, blue in the center where the light is most intense, then pink, then yellow in the region little exposed. When, however, the sample was exposed twice as long, with one-half the intensity, the original yellow color persisted. At first it was thought that the effect might be due to the warming and softening of the solvent by the intense beam. But this proved not to be the case (see experimental section), and semi-quantitative experiments finally showed that the amount of photochemical action (either to the pink or the blue luminescent form) is proportional to the time of exposure and to the *square* of the intensity of the light.

Such a photochemical process, which is of the second order with respect to photons, can most simply be interpreted as follows. The substances employed are not of the class that photo-oxidize directly at the light frequencies furnished by our mercury arc. However, if a considerable number of the molecules are in the phosphorescent state and one of these molecules receives the energy of a photon, this energy together with the great energy already present in the phosphorescent state would be ample to cause the ejection of a photon. In fact the processes just described occur with light at about 3600 Å. Since the number of molecules in the phosphorescent state, and also the number of such molecules that encounter new photons, are both proportional to the intensity of illumination, the amount of reaction would be proportional to the square of the intensity, as we have found it to be.

Returning to the dyes such as crystal violet and malachite green, the existence of a brilliant green phosphorescence in addition to the one lying chiefly in the infra-red seems to be the one remaining exception to the rule that for one substance there is a unique phosphorescent state. It is true that in both of these dyes there are isomers,[14] but the isomeric forms in each case differ so little from one another that the phosphorescence spectra should be nearly identical. There is, however, a pseudo-isomerism in such dyes, first discussed by Adams and Rosenstein,[18] and a similar pseudo-isomer was found in methylene blue.[19] Such pseudo-isomers differ from the parent molecule only by the addition of a molecule of solvent of the type ROH, from which the OR^-

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(16) von Kowalski, *Physik, Z.*, **12**, 956 (1911), and refs. therein.

(17) The yellow and blue proved to be true phosphorescences, while the pink luminescence could not be observed in the phosphoroscope, and therefore is either fluorescence, or phosphorescence of very short life. Almost identical phenomena were observed with α-naphthaldehyde and ethyl α-naphthoate. The results were the same in various solvents except that in glycerol, triethanolamine, and even in more fluid solvents, in the presence of the base, triethylamine, the pink luminescence did not appear and the change was directly from the yellow to the blue. We conclude, provisionally, that a substance like nitronaphthalene forms a dimer at very low temperatures, which, however, is not produced in the presence of a base, nor in a solvent which becomes rigid at so high a temperature that dimerization is inhibited on further cooling. The pink luminescence is then to be ascribed to the photo-oxidized dimer, the yellow to the original substance, presumably the monomeric form, and the blue to the photo-oxidized monomer.

(18) Adams and Rosenstein, THIS JOURNAL, **36**, 1452 (1914).

(19) Lewis, Goldschmid, Magel and Bigeleisen, *ibid.*, **65**, 1150 (1943).

adds to the central carbon, while H+ goes to one of the nitrogens. Such pseudo-isomers could be eliminated by the use of non-hydroxylic solvents, but so far we have found no such solvent that dissolves the dyes and also forms a glass at low temperature.

We have therefore used another method to demonstrate that the green phosphorescence is due to the pseudo-isomer; for the phosphorescence of the latter should be essentially the same as that of the carbinol. We have photographed the green phosphorescence spectrum of crystal violet carbinol and, except for slightly sharper band structure, due to our lower temperature, we find it identical with that obtained formerly[14] for the dye. In order to make this identification even more complete, we have obtained phosphorescence spectrograms of malachite green and malachite green carbinol, both in EPA at 90°K. shown in Plate II, 10a and 10b. It is evident that both of these identical green phosphorescence bands are to be ascribed to a carbinol type of molecule.[20]

Thus all of our experience indicates that for one substance there is only one phosphorescence state. However, if a molecule were divided into two independent resonating groups by some insulator, then we might expect to find two phosphorescent states. We shall later consider what may be one instance of this phenomenon, as well as another theoretically possible, but not yet experimentally demonstrated, exception to the rule.

4. **Character and Structure of the Phosphorescence Bands.**—Having concluded that the complicated phosphorescence bands of a single substance are due to processes involving a single phosphorescent state, we must see whether the various bands result from a drop from the phosphorescent state to different vibrational states of the normal molecule, or to states of vibration of the rigid solvent. Our experiments give a definite answer. We show in Fig. 2 microphotometer tracings of the phosphorescent spectra of carbazole (a) in dextrose glass at room temperature, (b) in glycerol at 193°K. and (c) in EPA at 90°K. Except for some temperature broadening, we see that the spectrum is independent of the solvent and belongs to the carbazole itself.[21]

Since we conclude that the several bands represent the fall from the phosphorescent state to a number of vibrational states of the normal molecule, and since the structure of a fluorescence spectrum is similarly interpreted, we might at first thought expect the two types of spectra to bear a marked resemblance to one another. Contrary to the conclusions of von Kowalski,[16] this is not in general the case. Figure 3 shows (simultaneously) the fluorescence and the phosphorescence of carbazole in EPA at 90°K. It is evident that neither in the general character nor in the degree of separation of the bands is there any resemblance.

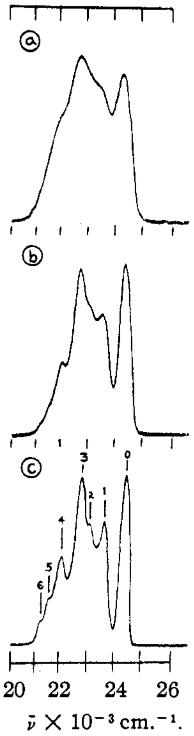

Fig. 2.—Tracing of photograph of phosphorescence spectrum of carbazole: (a) in dextrose at room temperature, (b) in glycerol at 193°K., (c) in EPA at 90°K.; showing the identity of the spectra in different solvents except for a temperature broadening. The peaks marked in (c) have the following frequencies in cm.$^{-1}$: 0, 24480; 1, 23650; 2, 23100; 3, 22820; 4, 22050; 5, 21550; 6, 21200.

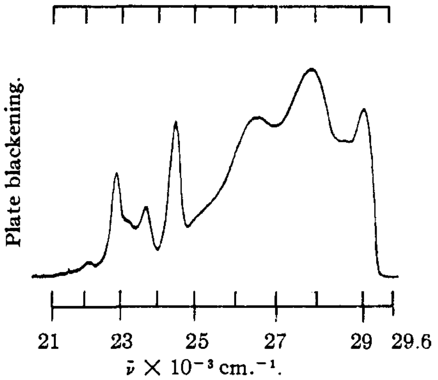

Fig. 3.—Tracing of the combined fluorescence (right) and phosphorescence (left, *cf.* Fig. 2) of carbazole in EPA at 90°K.; showing the far greater sharpness of the phosphorescence bands, as well as different intervals between bands.

Such a molecule has a great variety of possible vibrations, and, since the shape and size of the

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[20] These pseudo-isomers also give the clue to the mysterious extension of the x-absorption band system into the region from 24000 to 27000 cm.$^{-1}$ found for crystal violet, fluorescein, and rhodamine B (Lewis and Bigeleisen, THIS JOURNAL, **65**, 2102 (1943); **65**, 2107 (1943)). We are now convinced that the pure dye free from the pseudo-isomer would give no such bands.

[21] In our rigid solvents translation of large molecules is prohibited, as shown by the fact that no bimolecular reactions have been found. Even rotation of a molecule such as the ion of Wurster's Blue is imperceptible except at a temperature at which the solvent begins to lose its rigidity.[4] On the other hand, it seems probable that the rotation of small groups, as well as molecular vibrations, may occur without serious impedance.

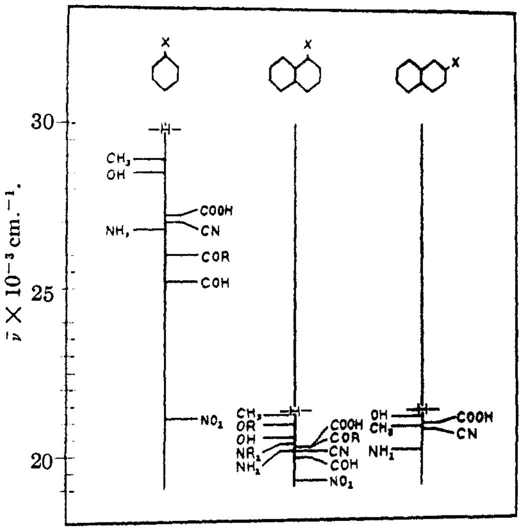

Fig. 4.—A tabulation of the highest frequency phosphorescence maxima of benzene, and benzene with one auxochrome substituent; also similar data for naphthalene with α- and β-substituents. Left, basic auxochromes; right, acid auxochromes.

molecule are presumably very different in the fluorescent and phosphorescent states, we should expect from the Franck–Condon principle that the most probable vibrations set up in the normal state would be quite different in the two cases. On the other hand in a nearly linear molecule, such as lycopene (Fig. 5), the separation of the bands is, within the limits of error, the same in fluorescence and phosphorescence.

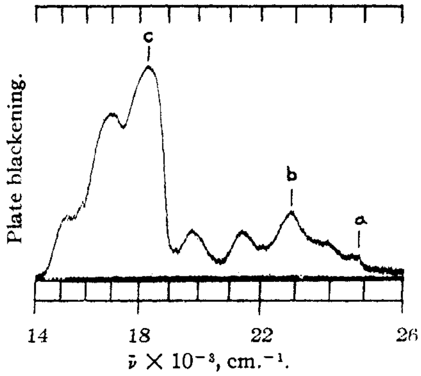

Fig. 5.—Phosphorescence spectrum of heat-treated lycopene: (a), 25000 cm.$^{-1}$; (b), 22900 cm.$^{-1}$; (c), 18300 cm.$^{-1}$.

As to *strength* of phosphorescence, we have not yet had the opportunity to determine the absolute quantum yield of phosphorescence for any substance. It must differ greatly for different substances under different conditions. When a substance absorbs light in passing to such a state as S′ in Fig. 1, many of the molecules may give out their energy in the form of fluorescent light and these molecules obviously play no part in producing phosphorescence. The remaining molecules in the S′ state go over into highly vibrating molecules of the S state[22] and these molecules would soon lose all their energy by dissipation, were it not that some of them on their way to the ground state find an opportunity of halting at the phosphorescent state. Even this fraction of the molecules that reach the phosphorescent state do not all give phosphorescence, for some return by the dissipative way and lose their energy as heat.

It is therefore not surprising that we find variations in the strength of phosphorescence and sometimes no phosphorescence at all. We have given no list of the substances which we have examined carefully for phosphorescence and which showed none. Some of the reasons for such failure to phosphoresce may be: (a) the substance may absorb too little of the exciting light employed; we believe that butadiene is an example. (b) The T state (Fig. 1) may lie above the S′ state, in which case it could not be produced from the S′ state, although perhaps it might from the S″ state; we believe that acetone is an example. (c) The fluorescence is very strong, in other words nearly all molecules reaching the S′ state return directly to S; *trans*-stilbene seems to belong to this class. (d) The substance may phosphoresce, but so far in the infra-red as not to be easily detected; in this way we are inclined to explain the non-phosphorescence of azobenzene and perhaps of benzalaniline. (e) The substance may phosphoresce, but the life of the phosphorescent state may be too short for our not very rapid phosphoroscope; we have proved this to be the case for thiobenzophenone.

It will be seen in the various photographs of Plate I that there is ordinarily a well-defined band of highest frequency with other bands extending toward the red, the number being limited only by the time of exposure and the sensitivity of the photographic plate. In order to see whether weak bands of higher frequency than those ordinarily observed might exist, the phosphorescence spectra of many substances were photographed with several hundred-fold over-exposure without showing any new bands of higher frequency, except in the one case of benzene.

The band of highest frequency, with a maximum intensity at a frequency which we shall henceforth designate as $\bar{\nu}_P$, corresponds approximately to the fall from the phosphorescent state to the vibrationless molecule in the normal state. So also we may write for the energy E_T of the phosphorescent state, taking the energy of the normal state as zero

$$E_T = hc\bar{\nu}_P \qquad (1)$$

Before regarding this equation as correct, we must consider the *width* of the phosphorescence bands. This width varies from substance to substance, but in all cases that we have investigated the phosphorescence bands (see Fig. 3)

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[22] Lewis, Magel, and Lipkin, THIS JOURNAL, **62**, 2973 (1940).

are much narrower[23] than the fluorescence bands, indicating that there is an uncertainty in the energy of the fluorescent state S′, far greater than in the normal state S, or in the phosphorescent state T.

Depending on the substance, the half-widths of the phosphorescence bands vary from less than 100 cm.$^{-1}$ to more than 1000 cm.$^{-1}$. Undoubtedly there is some broadening due to temperature and we have found that the bands may be narrowed by using, as a bath, liquid air boiling at about 60°K. under reduced pressure. Nevertheless, it seems there are other factors involved and that much of the breadth would persist even to the absolute zero. The width of the phosphorescence band shows some inefficiency in the emission process[24] and equation (1) is less accurate the broader the band. If $\Delta\bar{\nu}$ is the half-width, probably the best estimate of the energy of the phosphorescent state is expressed in the equation

$$E_T = hc(\bar{\nu}_P + \Delta\bar{\nu}) \qquad (2)$$

5. Employment of the Phosphorescence Spectrum in the Study of the Vibrational Levels of the Normal Molecule.—Since we are concerned in this paper primarily with the phosphorescent state, we shall at present enter upon no lengthy discussion of the band structures shown in the plates. Nevertheless, we must call attention to the powerful new tool furnished by the phosphorescence spectra for the investigation of the energy, and the proper assignment of the vibrational levels, of a molecule in its ground state. For it will be seen that levels of the vibrational states, concerning which little or no evidence is obtained from infra-red and Raman spectra, may be most prominent in phosphorescence spectra.

We may first point to the phosphorescence spectrum of **β-chloronaphthalene** (Plate I, 17) and its tracing (Plate II, 5). It is evidently very similar to that of **naphthalene** (Plate I, 1; Plate II, 2) associated with a very fine structure. Except for the halogen compounds, no such fine structure was found in the spectra of any of our other naphthalene derivatives and we may presume that it is, to a first approximation, due to a vibration of the halogen atom with respect to the rest of the molecule. At first we assumed, since all of the successive intervals are approximately equal, that all the fine structure was due to different quantum states of a single mode of vibration. However, **β-bromo-** and **β-iodonaphthalene** were later studied and while almost identical with β-chloronaphthalene, showed a marked alternation in the intensity of the bands, the bands 0 and 2 being about 20% more intense than bands 1 and 3. It may be, therefore, that the interval between bands 0 and 1 gives the frequency of one mode of vibration (perhaps bending) while the interval between bands 0 and 2 gives the frequency of another mode of vibration (perhaps stretching), which happens to be about double the former.

The first interval for β-chloronaphthalene of 280 cm.$^{-1}$ seems to correspond to a very weak band in the Raman spectrum of this substance, about 270 cm.$^{-1}$, found by Gockel.[25] The wave numbers for the first four bands for each of the three derivatives are given in Table I. The intervals both between bands 0 and 1 and between 0 and 2 decrease with the mass of the substituent, but not as much as would correspond to the change in reduced mass, if the force constants were equal. The spectra of the α-halogen naphthalenes were also studied. They are similar, but less simple, which may be due to a steric effect of the neighboring ring.

TABLE I

FIRST FOUR FINE BANDS OF MONOHALOGEN NAPHTHALENES (CM.$^{-1}$)

Band number	β-Chloro	β-Bromo	β-Iodo
0	21000	21100	21040
1	20720	20850	20820
2	20500	20620	20600
3	20200	20340	20280

There is no complex molecule whose modes of vibration have been so fully analyzed as those of **benzene**. For this reason, in spite of the very weak phosphorescence that benzene gives with our mercury arc, we have gone to some pains to obtain its complete phosphorescence spectrum (see notes to Plate II, 11). Before ever determining the frequencies of the several bands of benzene, we had concluded, for the reasons set forth in Section 8, that there must be a peculiar distortion of the benzene molecule in the phosphorescent state. Let us now attempt to ascertain the nature of this distortion. In the first place we may note that with most molecules the band of highest frequency is the strongest, or one of the strongest, of all. In the case of benzene the two bands of highest frequency are less intense by a factor of 20 to 100 than many of the other bands. We may apply the principle of **Franck**

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(23) In addition of the use of the phosphorescence bands in determining the vibrational levels of the normal state that we shall discuss in the next section, the sharpness and the unique pattern of the phosphorescence bands should make them of great service in the *identification* of substances in a mixture. Thus we show (Plate I, 6) a photograph of the phosphorescence of anthracene, from which other hydrocarbons have been removed, but which still contains a trace of carbazole (Plate I, 7, perhaps not evident in the reproduction). Moreover, the great difference between substances in the duration of phosphorescence will be of help. Thus we shall see that, with one exception, all the carbonyl compounds that we have studied have extraordinarily short lives.

(24) In the study of absorption and fluorescence there is always found a discrepancy between the peak of the absorption band of lowest frequency and that of the fluorescence band of highest frequency, this discrepancy becoming smaller when the bands are narrower. Here again the best estimate of the actual energy of the fluorescent state now available is obtained by averaging the two values of $\bar{\nu}$ and multiplying by hc. If the frequency of only one of the bands is known, a good guess at the energy may be obtained by adding or subtracting the half-width multiplied by hc.

(25) Gockel, *Z. physik. Chem.*, 29B, 82 (1935).

and Condon to the probability of transition between the phosphorescent state, which at the temperature of liquid air may be regarded as practically vibrationless, and the several vibrational levels of the normal state. Whenever the band of highest frequency, representing the fall to the zero vibrational level of the normal state is weak, it indicates that the molecule in the phosphorescent state differs widely from the molecule in the normal state in size or in shape.

Examining now the numerical values for benzene we see that bands 0 and 1 are separated by 500 cm.$^{-1}$, but this value is less accurate,[26] being obtained from a single plate, than any of the other separations. It could be in error by as much as 100 cm.$^{-1}$. In the list of frequencies and normal modes of vibration given by Pitzer and Scott[27] the two lowest frequencies are 400 cm.$^{-1}$ for mode 16 and 606 cm.$^{-1}$ for mode 6. Because of the repetition of this mode, noted below, we identify separation 0–1 with mode 16. There may be further bands of this series, but if so they are obscured by the bands of greater intensity, the first of which is at 28200 cm.$^{-1}$. This band 2 is separated from band 0 by 1625 cm.$^{-1}$. This interval is almost certainly to be identified with mode of vibration 8, which has been assigned a frequency of 1595 cm.$^{-1}$. As we proceed to the higher numbered bands the analysis becomes less certain, partly because of the reiteration of the mode 16 vibration and partly perhaps because of the appearance of frequencies belonging to other modes. However, it would be difficult to interpret bands 3, 4 and 5 except as representing 1 unit of mode 8, plus 1, 2, and 3 units of mode 16. The separations are 2-3 = 470 cm.$^{-1}$, 3-4 = 600 cm.$^{-1}$, 4-5 = 410 cm.$^{-1}$, averaging 460 cm.$^{-2}$. If the frequency for mode 16 is really only 400 cm.$^{-1}$ then it must be assumed that this frequency is increased when the molecule has one unit of vibration of mode 8.

If we look at the pictures[27] of the modes of vibration, especially 8A and 16B, we see that the former represents a stretching along an axis, and the latter a hinging motion about an axis. We may therefore picture the benzene molecule in the phosphorescent state as elongated (or compressed) along one axis, and bent out of the plane by hinging about this same axis.

We thus see that a study of the structure of the phosphorescence bands not only is important in bringing into prominence modes of vibration of the normal state, which are forbidden in infrared and Raman spectra, but it also tells much regarding the shape and size of the molecule in the phosphorescent state. Indeed the only selection rule here would seem to be that the vibrations prominent in the phosphorescence spectrum are those that would be observed if, let us say, a mechanical model for the normal state were distorted into a model of the phosphorescent state and then released.

6. **Chemical Constitution and the Energy of the Phosphorescent State.**—From now on we shall be concerned not with the complexities of band structure but only with the first band, at $\bar{\nu}_P$, whose frequency measures the energy of the phosphorescent state, as compared with the normal state of the molecule. Our experimental results based on photographs and their tracings, such as are exemplified in Plates I and II, and occasionally upon nearly equally accurate visual observations (see experimental section), are brought together in Table II. The first column shows the substance, and the second a rough estimate of the mean lifetime in the phosphorescent state (VS, < 0.01; S, 0.01–0.1; M, 0.1–1; L, 1–10; VL, > 10 seconds). The third column gives the values of $\bar{\nu}_P$; and the fourth, the energy in kcal. of the phosphorescent state, according to equation (1). In cases with very broad bands, 1, 2 or 3 kcal. have been added in accordance with equation (2), to obtain the corrected values of E_T, given in column five.

Before discussing the theory of the phosphorescent state, we shall present in this section some empirical observations concerning the effect of substituent groups upon the phosphorescence. The only previous attempt to ascertain the effect of substituents upon the phosphorescence spectra of organic molecules was that of von Kowalski,[16] who studied chiefly a number of substituted benzenes. Unfortunately his conclusions were vitiated by his belief that each substance has a definite number of phosphorescence bands, and by his choosing the frequency of the band of longest wave length for his theoretical considerations. However, his measurements of the high frequency bands seem accurate and several of these have been incorporated in Table II (marked K).

In Fig. 4 we compare the influence of several substituent groups on the values of $\bar{\nu}_P$ in the mono-substituted benzenes and the mono-substituted naphthalenes (alpha and beta positions). We find that the groups fall into essentially the same order in all three cases. In this figure we have separated the substituent groups which are basic auxochromes, from those that

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(26) We believe that the phosphorescence spectrum of benzene could be obtained with greater accuracy and perhaps with more structure. The true width of the bands is probably less than that shown on our plates. In order to obtain the two bands of highest frequency it was necessary to expose for thirty hours (E. K. III-O Plate) with a slit width of 0.5 mm. as compared with a 0.1 mm. slit usually used for strong phosphors. By using exciting light of higher frequency it would be possible to use a smaller slit width and a shorter exposure. A still further sharpening of the bands could be produced by using, as a bath, liquid air boiling under reduced pressure, say at 65°K. It would be better still to use liquid nitrogen for there is an oxygen absorption band at 27,800 cm.$^{-1}$. This, however, does not seem to have affected our spectrogram seriously. We hope that someone, more conversant with the problem of benzene vibrations than we are, will attack this problem and also the problem, suggested to us by Professor Redlich, of the phosphorescence of the deutero-benzenes.

(27) Pitzer and Scott, THIS JOURNAL, 65, 803 (1943).

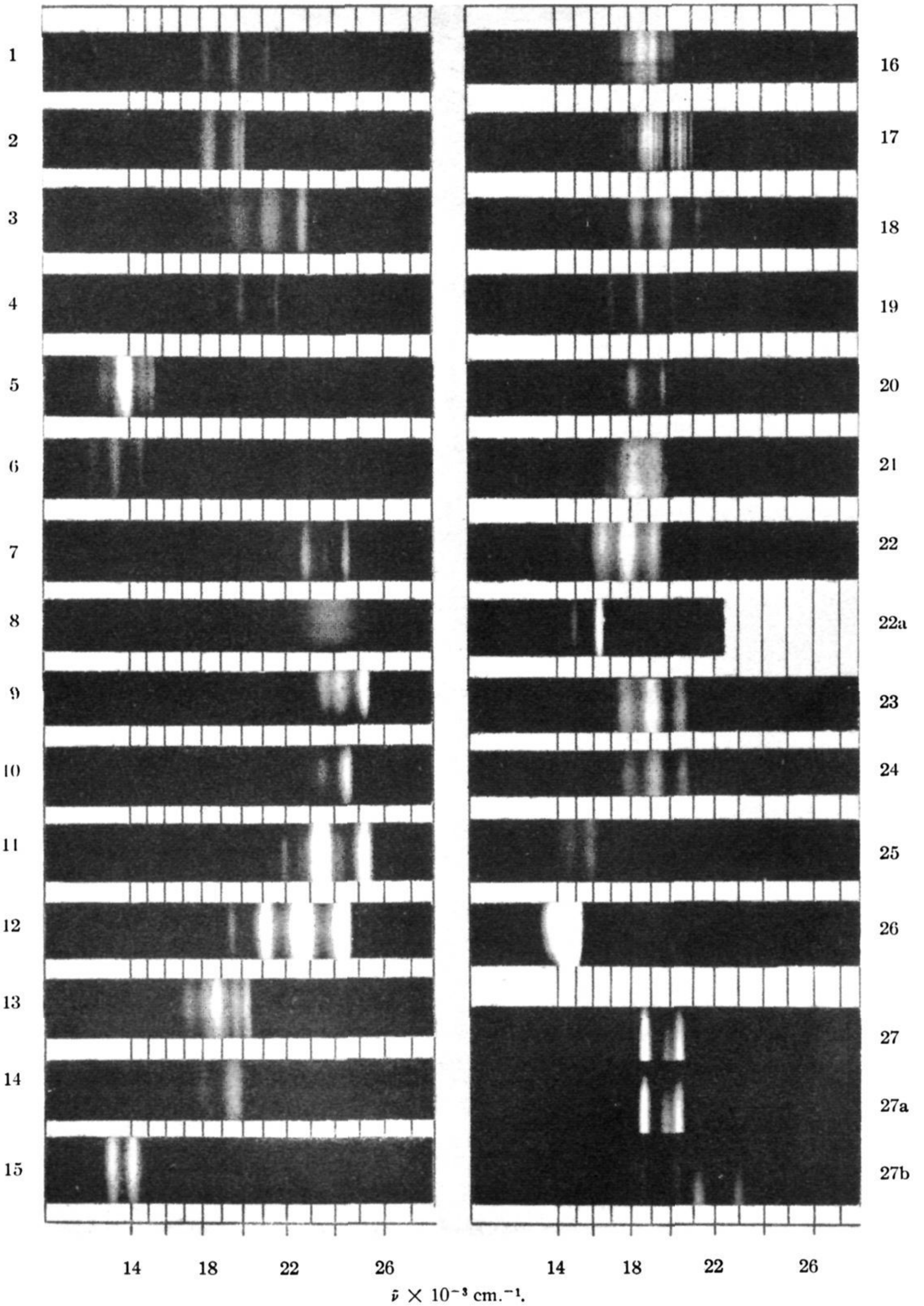

Plate I.—Photographs of the phosphorescence spectra of various substances, all in EPA at 90°K. (A comparison of some of these photographs with the corresponding tracings of Plate II will show that here there is some loss of detail in the reproduction.) 1, Naphthalene; 2, chrysene; 3, biphenyl; 4, *cis*-stilbene; 5, phenazine; 6, anthracene; 7, carbazole; 8, *p*-dimethyltoluidine; 9, diphenylamine; 10, triphenylamine; 11, benzaldehyde; 12, benzophenone; 13, methyl-α-naphthyl ketone; 14, biacetyl; 15, thiobenzophenone; 16, α-chloronaphthalene; 17, β-chloronaphthalene; 18, α-methylnaphthalene; 19, α-naphthonitrile; 20, α-naphthaldehyde; 21, *p*-nitroaniline; 22, α-nitronaphthalene; 22a, the pink luminescence obtained after intense illumination of α-nitronaphthalene; 23, 4-nitrobiphenyl; 24, 2-nitrofluorene; 25, *t*-4-nitrostilbene; 26, eosin; 27, anthraquinone; 27a, same after illumination; 27b, same after prolonged illumination.

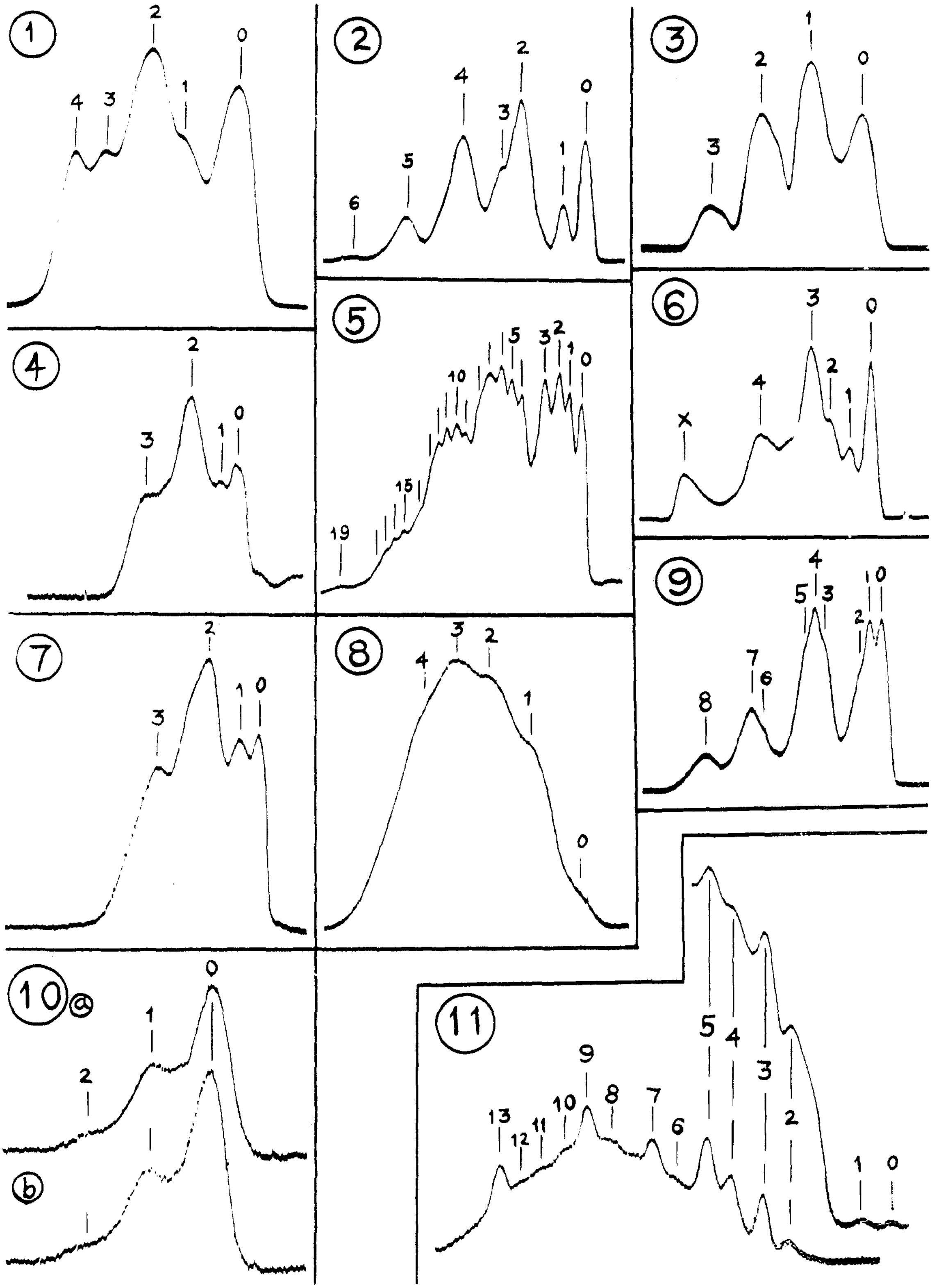
①
4 3 2 1 0
②
6 5 4 3 2 1 0
③
3 2 1 0
④
3 2 1 0
⑤
19 15 10 5 3 2 1 0
⑥
x 4 3 2 1 0
⑦
3 2 1 0
⑧
4 3 2 1 0
⑨
8 7 6 5 4 3 2 1 0
10 ⓐ
2 1 0
ⓑ
⑪
13 12 11 10 9 8 7 6 5 4 3 2 1 0

Plate II.

Plate II.—Microphotometer tracings of phosphorescence spectra.* After the substance, is given the plate used, slit width of spectrograph, followed by the exposure time. The band number and its position (cm.$^{-1}$) appear next.

1. *sym.-trans*-Dibromoethylene: III-O, 0.50 mm., 1 hr.
   0, 25200 1, 24140 2, 23500 3, 22600
   4, 21940
2. Naphthalene: III-F, 0.50 mm., 1 hr.
   0, 21300 1, 20800 2, 19830 3, 19420
   4, 18450 5, 17050 6, 15700
3. α-Nitronaphthalene: III-F, 0.40 mm., 6 min.
   0, 19200 1, 18000 2, 16750 3, 15350
   Bands 2 and 3 show evidences of oxygen absorption u and v (Fig. 6).
4. Anthracene: I-N, NH_3 sens., 0.50 mm., 5 hr.
   0, 14700 1, 14200
   The apparent structure at the right is due to the oxygen absorption band v (Fig. 6).
5. β-Chloronaphthalene: 103-F, 0.10 mm., 40 sec.
   0, 21000 1, 20720 2, 20500 3, 20200
   4, 19680 5, 19450 6, 19190 7, 18850
   8, 18650 9, 18300 10, 18100 11, 17830
   12, 17600 13, 17400 14, 17200 15, 16700
   16, 16500 17, 16300 18, 16000 19, 15000
6. α-Naphthaldehyde: III-F, 0.20 mm., 10 min.
   0, 19850 1, 19350 2, 18850 3, 18350
   4, 17100
   The band marked X is due to Pyrex and begins at 15900, with an apparent peak at 14900, and ending abruptly at 14500 due to falling off in the plate sensitivity.
7. Phenazine: I-N, NH_3 sens., 0.50 mm., 3 hr.
   0, 15250 1, 14700 2, (13800)
8. Aniline: III-O, 0.40 mm., 20 min.
   0, 26500 1, 25600 2, 24900 3, 24200
   4, 23500
9. Chrysene: 103-F, 0.20 mm., 3 min.
   0, 20000 1, 19700 2, 19500 3, 18600
   4, 18400 5, 18200 6, 17050 7, 16700
   8, 15500
   Many fine intermediate bands upon longer exposure. Some resolution was lost in use of a too large tracing slit.
10. a. Malachite green carbinol; b, Malachite green (green band): 103-F, 0.20 mm., 30 sec.
    0, 21400 1, 20000 2, 18600
11. Benzene: Upper photograph, III-O, 0.50 mm., 30 hr.; lower photograph, III-O, 0.50 mm., 4 hr.
    0, 29825 1, 29325 2, 28200 3, 27730
    4, 27130 5, 26720 6, 26180 7, 25690
    8, 24950 9, 24470 10, 24000 11, 23600
    12, 23200 13, 22700
    Except for the two highest frequencies, photographs were also made with a 103-F plate, which showed no departure from the results with III-O. Several tracings from both types of plate were averaged in the above data.

* In the case of broad bands, especially in the red and infra-red, the maximum of the tracing curve does not quite correspond to $\bar{\nu}_P$, because of lack of uniformity of sensitization of the plate at different wave lengths. We have determined the plate characteristics, but have not so far made the appropriate corrections, because of the other uncertainties in the calculation of E_T from broad bands.

are acid auxochromes, and it will be seen that they fall into the same order as that found for their effect upon the color of dyes.[28] The reason for this parallelism will later be evident. However, it is to be noted that while OR and NR_2 are stronger color auxochromes than OH and NH_2, respectively, this difference is not found in our table.

In color theory the most powerful acid auxochrome is the **nitroso** group. Unfortunately we have not had opportunity so far to study the phosphorescence of these interesting compounds, but we shall see in section eight[38] that we may expect the nitroso group to lower very greatly the energy of the phosphorescent state.

One of the characterizing features of each phosphorescence is the average life of the phosphorescent state. It is a remarkable fact, for which at present we have no explanation, that the substances with a carbonyl group invariably have short lives for the phosphorescent state. Next come the nitro-bodies, while most of the remaining substances have phosphorescence of longer life. It also seems that within a given class the life is shorter when the phosphorescence is in the red or infra-red, as in the cases of phenazine and crystal violet.

While most of our observations have been made upon aromatic substances, Table II includes several much simpler substances, such as the halogen substituted ethylenes and di-isopropyl ketone. Nor is the phosphorescence of our rigid solutions limited to organic substances; carbon dioxide, sulfur dioxide and other *inorganic substances* in rigid EPA show similar phosphorescences. We have postponed a detailed study of inorganic substances and some of the simpler organic substances until we can use exciting light of higher frequency than that furnished by the high pressure mercury arc. We wish, however, to emphasize the great generality of the phenomenon of phosphorescence in unsaturated molecules.

7. Identification of the Phosphorescent State with the Triplet or Biradical State.[29]

—It was formerly supposed that the long life of the phosphorescent state, as compared with the fluorescent state, was to be ascribed to a quasi-prohibition of the radiative fall from the phosphorescent state to the normal state. Such prohibition and quasi-prohibitions are frequently met in the study of atomic spectra. The only such prohibition that could be expected in a complex molecule would be

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(28) See Wizinger, "Organische Farbstoffe," F. Dümmlers Verlag, Berlin, 1933.

(29) The physicist speaks of the triplet state, the organic chemist of the biradical state. The triplet state implies a pair of electrons with spins parallel; a substance that has two "odd" electrons is called a biradical. The two names are synonymous except that in the organic biradicals their two odd electrons may be sufficiently insulated from one another that their spins are independent of each other.

TABLE II

PHOSPHORESCENCE DATA

	Substance	Life	$\bar{\nu}_{\mathrm{P}}$, cm.$^{-1}$	E_{T} by Eq. 1, kcal.	E_{T} by Eq. 2, kcal.
	Ethylene Derivatives				
1	Ethylene		25000	72	74
2	*sym-trans*-Dichloroethylene	L	25300	72	74
3	*sym-trans*-Dibromoethylene	M	25200	72	74
4	*sym-trans*-Diiodoethylene	L	25100	72	74
5	Lycopene (main band)	VL	18300	52	54
6	Hexachlorobutadiene	L	25800	74	75
7	*cis*-Stilbene	L	21700	62	
	Hydrocarbons and Nitrogen Analogs				
8	Benzene	L	29800	85	
9	Naphthalene	L	21300	61	
10	Chrysene	L	20000	57	
11	Anthracene		14700	42	
12	Phenazine	S	15300	44	
13	Biphenyl	VL	22800	65	66
14	Quinoline	L	21700	62	
	Amines				
15	Aniline	VL	26800	77	80
16	Diphenylamine	L	25200	72	74
17	Triphenylamine	VL	24500	70	72
18	α-Naphthylamine	L	20100	58	59
19	β-Naphthylamine	L	20100	58	59
20	Dimethyl-α-naphthylamine	L	20300	58	61
21	Phenyl-β-naphthylamine	L	20200	58	60
22	Di-β-naphthylamine	L	19800	57	59
23	2-Aminofluorene	VL	22700	65	
24	Carbazole	VL	24500	70	
25	1,8-Diaminonaphthalene	L	19100	55	
	Nitro Compounds				
26	Nitrobenzene	M	21100	60	63
27	α-Nitronaphthalene	M	19200	55	58
28	2-Nitrofluorene	M	20600	59	62
29	2-Nitrobiphenyl	M	20800	60	63
30	4-Nitrobiphenyl	M	20500	59	62
31	*t*-4-Nitrostilbene	M	17400	50	51
32	1,5-Dinitronaphthalene	M	19900	57	59
33	1,8-Dinitronaphthalene	M	20000	57	59
34	4,4'-Dinitrobiphenyl	M	20200	58	61
35	8-Nitroquinoline	M	20200	58	61
36	3-Nitrodiphenylene oxide	M	19800	57	60
37	*p*-Nitroaniline	L	19300	55	58
38	1-Nitro-2-aminonaphthalene	M	19300	55	58
39	1-Nitro-5-aminonaphthalene	M	17900	51	54
40	*m*-Nitroacetophenone		20300	58	61
41	1-Nitro-2-methylanthraquinone		20700	59	62
	Aldehydes and Ketones				
42	Benzaldehyde	S	25200	72	75
43	α-Naphthaldehyde	M	19900	57	
44	Acetophenone	M	26000	74	76
45	Benzophenone	S	24400	70	73
46	Thiobenzophenone	VS	14100	40	43
47	Methyl α-naphthyl ketone	S	20200	58	59
48	Michler ketone	L	21700	62	65
49	Dibenzalacetone	S	18500	53	56
50	Benzil	S	21600	62	65
51	Biacetyl	VS	19700	56	58
52	Acetyl propionyl	VS	18600	53	55
53	Di-isopropyl ketone	VS	25900	74	77
54	Anthraquinone	S	20400	58	59
	Other Benzene Derivatives				
55	Toluene (K)		28900	83	
56	Phenol (K)		28500	82	
57	Benzonitrile (K)		27000	77	
58	Benzoic acid	L	27200	78	80
59	*p*-Dichlorobenzene	S	26000	74	77
	Other Naphthalene Derivatives				
60	α-Methylnaphthalene	L	21200	61	
61	β-Methylnaphthalene	L	20800	60	
62	α-Chloronaphthalene	L	20700	59	
63	β-Chloronaphthalene	L	21000	60	
64	α-Bromonaphthalene	L	20700	59	
65	β-Bromonaphthalene	L	21100	60	
66	β-Iodonaphthalene	L	21040	60	
67	α-Naphthol	L	20500	59	
68	β-Naphthol	L	21100	60	
69	Methyl α-naphthyl ether	L	20900	60	
70	α-Naphthoic acid	L	20200	58	
71	β-Naphthoic acid	L	20900	60	
72	Ethyl α-naphthoate	L	20100	58	
73	α-Naphthonitrile	L	20100	58	
74	β-Naphthonitrile	L	20700	59	
75	Thio-β-naphthol	L	20800	60	
	Quinoline Derivatives				
76	8-Methylquinoline	L	21300	61	
77	2,4-Dimethylquinoline	L	21800	62	
	Other Biphenyl Derivatives				
78	2,2'-Difluorobiphenyl	L	24400	70	72
79	4,4'-Difluorobiphenyl	VL	23000	66	68
80	2,2'-Dichlorobiphenyl	L	25000	72	74
81	2,2',6,6'-Tetrachlorobiphenyl	L	24500	70	72
82	2,2',4,4',6,6'-Hexachlorobiphenyl	L	23200	66	68
	Miscellaneous				
83	Di-α-naphthylurea	L	20200	58	59
84	(Acid) Fluorescein[10]	L	17700	51	54
85	Crystal violet carbinol	M	21300	61	63
86	Crystal violet[14]	S	13600	39	42
87	Malachite green carbinol	L	21400	61	63
88	Eosin	VS	14900	43	46
89	Acridine yellow	L	20200	58	61

the one against a transition between two states of different multiplicity. In the ordinary case this would mean that the phosphorescent molecule is in a triplet state. On the other hand, it has been suggested by Franck and Livingston[30] that the molecule in the phosphorescent state is a tautomer of the normal molecule, the change to the normal state being inhibited by the forces present in a rigid medium. The phosphorescent state might, by a generalization of this idea, be merely a distorted form of the normal molecule. These theories were discussed by Lewis, Lipkin, and Magel,[10] without a definite conclusion being reached. One of their observations, however, seems to us now nearly decisive. Referring again to Fig. 1, it was shown that molecules in the phosphorescent state T could by light absorption go to states T′ and T″, always returning to the state T. This could be easily understood if the states S, S′ and S″ belong to one set, and the states T, T′ and T″ to another set, not combining with the first because of a difference in multiplicity. On the other hand, since in the absorption to the T′ and T″ states much vibrational energy is set free, producing a local heating in the neighboring solvent, it would seem unlikely that all or most of the molecules would return to the T state, if the rigidity of the solvent were the determining factor.

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(30) Franck and Livingston, *J. Chem. Phys.*, **9**, 184 (1941); see also Franck and Pringsheim, *ibid.*, **11**, 21 (1943).

If the relatively long life of the phosphorescent state is to be ascribed to a quantum mechanical prohibition, why is phosphorescence limited to rigid systems? The answer is that it is not so limited. In another paper soon to follow we shall find in fluid solvents at room temperature several instances where we can measure a quasi-forbidden absorption band which represents the opposite of the phosphorescence emission, namely, a transition from the S to the T state. We shall also give examples of phosphorescence in liquid and even in gaseous media, and show that the phosphorescent state is identical with that in a rigid solvent.

The fact that phosphorescence is ordinarily seen only in rigid media is to be explained as follows. Even at low temperatures, where the alpha process is negligible, the beta process is not the only one by which a molecule may pass from the phosphorescent to the normal state. It may also descend by a non-radiative dissipative process, in which the energy is given up as thermal energy. The rate of disappearance of the phosphorescent molecules is the sum of the rates of the beta process and the dissipative process, and only in the limiting case, when the latter process is negligible, is the life of the phosphorescent state determined by the beta process alone.

If any strong phosphor is gradually warmed, its phosphorescence gradually diminishes in intensity, but may often still be seen at a temperature at which the solvent has become a pourable liquid. As the fluidity increases, and the phosphorescent intensity diminishes, the life of the phosphorescent state also diminishes markedly; a rise in temperature of only a few degrees may diminish the life by a factor of ten. It is evident that with increasing fluidity there is an increasing quenching. It is not that the nature of the phosphorescent state, nor of the beta process, is being affected, but that the dissipative process is becoming the rate-determining process. In other words the main function of rigidity is to protect the molecules in the phosphorescent state from the process of dissipation.

Having concluded, therefore, that the existence of the phosphorescent state is not contingent upon a rigid solvent, there seems no reasonable alternative to the assumption that the phosphorescent state is the triplet state of the molecules. It remains to test this assumption in as many ways as possible. Since the triplet state must always possess a magnetic moment, it should show a measurable paramagnetic susceptibility. We hope soon to report experiments, which are now in progress, upon the susceptibility of substances in the phosphorescent state. Here, however, in the next section, we shall consider only the chemical evidence, which in itself seems sufficient to require the identification of the phosphorescent state with the triplet state.

While we are to identify the phosphorescent and triplet states for the ordinary molecule, which is normally in the singlet state, conditions are reversed for those molecules whose normal state is triplet, whereas the singlet belongs among the excited states. Such molecules are a number of organic biradicals, and molecular oxygen. Here phosphorescence will be associated with the slow fall from the lowest singlet to the lowest triplet state. It has been estimated[31] that the excited singlet oxygen molecule lives for several seconds, before its return to the ground state.

In these cases an energy diagram such as that in Fig. 1 will show the lowest S level above the lowest T level. In all cases the *normal* processes of absorption and emission will be between one S level and another S level, or between two T levels. *Abnormal* or quasi-forbidden absorption and emission will be between an S and a T level. We are now in a position to distinguish sharply between *fluorescence* and *phosphorescence*. Fluorescence is the light emitted in falling from an S level to an S level, or from a T level to a T level. Phosphorescence is the light emitted when the molecule falls from a level of one class to a level of the other class. What has been called alpha phosphorescence is essentially fluorescence, since a molecule in the phosphorescent state has been thermally activated to a state of the same class as that to which it is about to fall.

8. Chemical Evidence for the Identity of the Phosphorescent and Triplet States.—In a saturated molecule, such as methane or ammonia, it would be impossible to change one of the normal electron-pairs into two electrons of parallel spin, all within the regular valence shell. According to the Pauli principle one of the electrons would have to go into an outer shell and this would require a large energy. Thus we may ordinarily expect to find the triplet state only in molecules with incomplete valence shells, *e. g.*, BR_3 and C_2H_4. Molecules of the latter type, with one or more double bonds, are the ones with which this paper deals.

The energy of the triplet state of ethylene has been the subject of previous inquiries. Some authors,[32,33] in order to account for certain rates of isomerization about the double bond, have assumed that one mechanism of isomerization is through the triplet state. Thus for several olefinic substances, they assume that the triplet state has about 20 kcal. more energy than the normal state. On the other hand, Hartmann[34] has made a quantum mechanical calculation of the energy of the triplet state of ethylene, and finds 72 kcal.[35]

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(31) Childs and Mecke, *Z. Physik*, **68**, 344 (1931).

(32) Tamamusi and Akujama, *Z. Elektrochem.*, **43**, 156 (1937).

(33) Magee, Shand and Eyring, THIS JOURNAL, **63**, 677 (1941).

(34) H. Hartmann, *Z. physik. Chem.*, **135B**, 96 (1943).

(35) This nearly agrees with our experimental value of 74 kcal., but we think it should not, for Hartmann assumes a triplet state in which the two carbons are at the same distance as in normal ethylene. We believe that in the actual triplet state the separation is much greater, greater even than the single bond distance, and therefore that his calculation should have given a considerably higher value for the energy.

We may begin our theoretical discussion of triplet state energies by considering the familiar tables of bond energies.[36] When the molecule $H_2C{=}CH_2$ goes over into the triplet state, we may represent the latter as

$$H_2\overset{*}{C}{-}\overset{*}{C}H_2$$

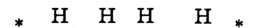
where the asterisks represent the two odd electrons with parallel spin. The process is not unlike that in which a molecule breaks a single bond to give two free radicals. In the latter case the energy required for dissociation is a little greater[37] than the bond energy ordinarily assigned. The difference between $C{=}C$ and $C{-}C$ is 41 kcal. and we might expect a slightly larger value, say 45 kcal., for the energy of the symmetrical breaking of one member of the double bond to give the triplet molecule. In fact, this is the value that we have provisionally chosen for this basic process.

However, we cannot hope from this figure alone to obtain the triplet state energy for such a molecule as ethylene. In the case of the hydrogen molecule, which has been so successfully treated by quantum mechanical methods, it takes some 200 kcal. to change from the normal state to the triplet state, if the two atoms have the same distance as in the normal molecule. This corresponds to a great repulsive force, which falls off rapidly as the atoms are separated. In the case of ethylene, after breaking one member of the double bond, the two halves cannot fly apart, being held by the remaining member. It seems probable, however, that this repulsion will make the distance not only greater than that of the double bond, between carbon and carbon, but even greater than that of the single bond. There will remain an energy of repulsion which we are unable to calculate, but must determine experimentally.

We have not had available radiation of high enough frequency to study directly the phosphorescence of ethylene, but we have studied *sym-trans*-dichloro-, dibromo- and diiodoethylene, all of which give nearly identical values for $\bar{\nu}_P$, corresponding to 74 kcal. (corrected), as seen in Table II. We may assume that this is approximately the value for ethylene also, and indeed we shall mention presently an experiment in which we very likely have an ethylene phosphorescence at this same value.

If we subtract from this 74 kcal. the 45 kcal. that we have assigned to the pure breaking of a double bond to form the triplet state, we have 29 kcal. which we may call the *repulsive energy* in the triplet state of ethylene. In most molecules, in which the two electrons of parallel spin can move much farther from one another than in ethylene, we consider that this repulsive energy disappears.

When a complicated molecule is in the triplet state, we may expect to find superposed upon ordinary resonance a special type of resonance due to the ability of the odd electrons to take up different positions within the molecule. However, in the case of ethylene we can write only the one reasonable formula given above.[38] The same is probably nearly true of the **polyenes,** for not only do the two odd electrons tend to separate, to diminish the repulsive energy, but, in an all-*trans* chain, any disposition of the odd electrons except in the ω, ω' positions would interfere with the normal resonance by breaking the polyene into insulated parts. We shall therefore consider that the only important formula of the triplet state is



$$H_2\overset{*}{C}{-}\overset{H}{C}(={\overset{H}{C}}{-}\overset{H}{C})_n{=}\overset{H}{C}{-}\overset{*}{C}H_2$$

We have made a number of experiments with **lycopene**. For some reason that we do not understand the all-*trans* form shows very little phosphorescence or fluorescence. However, after a short heat-treatment to produce some of the *cis* forms[39] we obtained a photograph of the phosphorescence spectrum, a tracing of which is shown in Fig. 5, which seems to contain several band systems. Within each system the separation of the bands is approximately the same as that of the fluorescence bands of the polyenes, as found by Hausser, Kuhn and Kuhn.[40] After the solution had stood several months in the dark and in a vacuum, at room temperature, a still more complicated set of phosphorescence bands was found.

While much more work will be necessary for a complete analysis, we may now make a provi-

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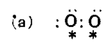
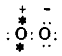
(36) We shall use the data given by Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940.

(37) Lewis and Lipkin, THIS JOURNAL, 63, 3232 (1941).

(38) Conditions are quite otherwise in the triplet state of the oxygen molecule. We may assume that the bonding electron pair takes no part in the odd-electron resonance; but in oxygen there are many non-bonding electrons, any two of which may have the parallel spins that characterize the triplet state. In some of the possible forms the odd-electrons may be on different atoms, as illustrated in formula (a). In others they are on the same atom, as in formula (b).

(a)  (b) 

That the latter unsymmetrical or polarized forms contribute largely to the resonance, is shown by the fact that, in spite of the repulsive force, the atoms in triplet oxygen are much closer together than in an ordinary molecule with a single bond between two oxygen atoms. There are six of these unsymmetrical forms and nine of the symmetrical forms. All these opportunities of resonance undoubtedly explain the low energy of triplet oxygen.

Consider the series $O{=}O$, $RN{=}NR$, $R_2C{=}CR_2$: the second of these has four symmetrical and two unsymmetrical forms. We may guess therefore that E_T will lie between the -23 kcal. for oxygen and the $+74$ kcal. for ethylene, and nearer the latter. We have mentioned that the phosphorescence of azobenzene probably lies in the infra-red beyond the limit (11600 cm.$^{-1}$) of our photographic plate (E. K. I-L), while *cis*-stilbene has $\bar{\nu}_P$ = 21700 cm.$^{-1}$. When the double bond is between two unlike atoms, the class with lowest E_T should be the nitroso compounds, $RN{=}O$. It seems likely that the pale blue or green color of these compounds is due to a quasi-forbidden transition from the S to the T state. We shall discuss several similar problems in our next paper.

(39) Zechmeister, LeRosen, Schroeder, Polgár and Pauling, THIS JOURNAL, 65, 1940 (1943).

(40) Hausser, Kuhn and Kuhn, *Z. physik. Chem.*, 29B, 417 (1935).

sional and apparently not unreasonable assignment of some of these bands. The left-hand series (c) with $\bar{\nu}_P = 18300$ cm.$^{-1}$ ($E_T = 52$ kcal.) we may assign to some, and probably to any long straight polyenic chain, even though this is only the straight portion of a partly *cis* molecule.[41]

Let us set up the formula

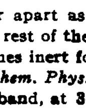
$$E_T = B + \rho + \Delta E_R \qquad (3)$$

where B is the value for the breaking of a double bond, which for C=C we have taken as 45 kcal.; ρ is the repulsive energy, which, except for small molecules like ethylene, may be neglected; ΔE_R represents the resonance energy in the singlet state, less the resonance energy in the triplet state. Using the value that we have just assigned to a long straight polyenic chain, we find $\Delta E_R = 52 - 45 = 7$ kcal. This is a reasonable value, since we have assumed that there is no odd-electron resonance, and therefore the resonance energy of the triplet state is that of a normal polyene, with one double-bond less than in the original molecule.

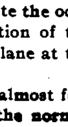
The band series beginning at (b) (Fig. 5) we shall tentatively assign to some short polyenic chain. Finally we must consider the remarkable band (a) at 25000 cm.$^{-1}$. This coincides with the value that we have assumed for ethylene. Lycopene has at each end an unconjugated double bond and it would seem that, during the excitation of the whole molecule, occasionally one of these isolated portions has been driven into the triplet state. If this is true, we have an exception to our rule that a substance has only one phosphorescent state, and such exceptions may be expected whenever a molecule consists of parts that are insulated from one another.

Of all the substances we have investigated, **benzene** has the highest value[41a] of $\bar{\nu}_P$ (29800 cm.$^{-1}$ = 85 kcal.). Also we have seen that benzene (Plate II, 11) has phosphorescence bands of an unusual character. Many formulas could be written for triplet benzene. We may discard the six forms in which the two odd-electrons are *ortho* to each other, since such forms would have a high value for the repulsive energy, ρ. There remain three *para* forms which might be expected to resonate freely with one another.[42] However, if we apply equation (3), taking $\rho = 0$, we find $\Delta E_R = 85 - 45 = 40$ kcal.; but this is approximately equal to the known resonance energy of singlet benzene. In other words, the resonance energy in the triplet state is nearly zero. This remarkable fact can best be interpreted by assuming that there is so great a distortion of the molecule, in the triplet state, that the change from one *para* form to another would be associated with too great atomic displacements to permit resonance (see Pauling,[36] p. 426).

Ortho forms:



Para forms:



Let us consider, *a priori*, what we might expect for the size and shape of a molecule of triplet benzene with odd-electrons in the 1,4 positions. The distances between carbons 2 and 3 and between carbons 5 and 6 will be slightly shortened, since these pairs are now connected by true double-bonds. All the other bonds, being now pure single-bonds, will be greatly lengthened, thus producing a considerable total elongation along the 1,4 axis. In other words, the dimensions should approximate those of 1,4-dihydrobenzene. Unlike the latter, however, the 1,4 carbons in triplet benzene are attached to one hydrogen and one odd-electron each. Since there is here no obstacle to a bending out of the plane about the 1,4 axis, such bending presumably will occur until the most favorable bond angles are reached. We thus have a picture of triplet benzene which is identical with the one that we have already deduced from the structure of the phosphorescence spectrum.

If these views of triplet benzene are correct, it would imply a second exception to our rule that there is only one phosphorescent state, for if we had considered toluene instead of benzene we should have two *isomeric* forms of the triplet molecule, according as one of the odd electrons is, or is not, at the substituted position.

Naphthalene gives $\Delta E_R = 61 - 45 = 16$ kcal. This small value, considering the large amount of normal naphthalene resonance that must be destroyed in forming the triplet state, indicates that there is considerable odd-electron resonance in the triplet state, which would be incompatible with the type of distortion found in benzene. Indeed, the band of highest frequency (Plate I, 1; Plate II, 2) is sharp and strong, showing a high probability of direct transition from the triplet state to the normal state without vibration. We may conclude that the singlet and triplet states are approximately of the same size and shape.

We next consider **anthracene,** the study of the phosphorescence of which, in the early stages of our work, gave us the first assurance that the phosphorescent state is a triplet state. Pringsheim[1] pointed out the remarkable fact that while phenanthrene and many other polynuclear

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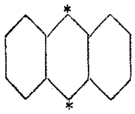
[41] We shall see that the triplet state is very sensitive to small steric effects. Thus hexachlorobutadiene (Table II, No. 6) has a triplet state energy the same as that of ethylene, instead of the lower value that we expect for a diene. Such steric effects we shall find also in the *o*-substituted biphenyls. A polyene molecule at a *cis* point is under a strain that tends to force one part of the molecule out of the plane. We are assuming that in the triplet state the odd-electrons are as far apart as possible in a straight portion of the molecule, while the rest of the molecule goes out of the plane at the *cis* point and becomes inert for resonance.

[41a] Sklar, *J. Chem. Phys.*, **5**, 669 (1937), assigns an almost forbidden absorption band, at 3400 Å., to transition from the normal singlet to a triplet state. This would make E_T = 84 kcal.

[42] In discussiong the resonance of triplet molecules we pay no attention at present to the resolution of the members of the triplet, such as might be produced by a magnetic field.

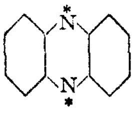
hydrocarbons showed strong phosphorescence, it had never been found in pure anthracene. Now anthracene and some of its derivatives, under the influence of light and heat, show certain reactions such as peroxide formation, and the production of dianthracene. These reactions have been explained on the assumption of a biradical or triplet state as an intermediate step. We were thus led to the suspicion that anthracene would show a phosphorescence, but, the triplet state being of low energy, that this phosphorescence would be in the infra-red. For this reason we made our first experiments with an infra-red sensitized spectrographic plate (Plate I, 6; Plate II, 4), and immediately found the characteristic bands of anthracene beginning at 6800 Å. or $\bar{\nu}_P = 14700$ cm.$^{-1}$ ($E_T = 42$ kcal.).

Applying our formula (3) and again taking $\rho = 0$, we find a small negative value for ΔE_R, namely, -3 kcal. A value not far from zero is to be expected, since we may write, as the main resonating form, the one with the odd electrons in the 9, 10 positions, as

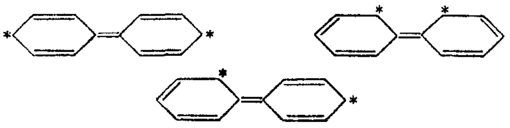


Fixing the odd electrons in the 9,10 positions we still have four forms due to Kékulé resonance and this is the same number of main resonance forms that exist in the singlet state.[36] There undoubtedly is, however, some loss of ordinary resonance energy in the triplet molecule, but it seems that this is a little more than compensated by a small resonance in the triplet state, with forms in which the odd-electrons are in other than the 9,10 positions. No phosphorescence was found in *9,10-diphenylanthracene*. Undoubtedly $\bar{\nu}_P$ lies too far in the infra-red for us to measure.

Phenazine has the same electronic pattern as anthracene and the same considerations apply. In fact, the spectrum (Plate I, 5; Plate II, 7) is almost identical with that of anthracene, but with a slightly higher $\bar{\nu}_P$, 15300 cm.$^{-1}$, so that its red phosphorescence is observable visually. Here again by far the most important resonating form of the triplet state is undoubtedly

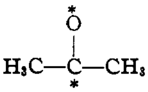


One of the most striking confirmations of the identification of the phosphorescent and the triplet states came in the study of **biphenyl** and its derivatives. Here, in going to the triplet state we should expect, not the breaking, but the production of a central double bond to give various forms such as



If, therefore, the energy of the triplet state is greatly lowered by the existence of these forms, we should expect a great increase in $\bar{\nu}_P$ if the central double bond is inhibited, namely, by the well-known steric effect of *ortho* substituents. For biphenyl itself the value of $\bar{\nu}_P$ is 22800 cm.$^{-1}$, far below that for benzene. Our first experiments upon substituted biphenyls were with 4,4′ and with 2,2′-difluorobiphenyl. In the first case $\bar{\nu}_P$ is 23000 cm.$^{-1}$, hardly distinguishable from that for biphenyl itself. However, with two *ortho* fluorines, $\bar{\nu}_P$ was found to be 24400 cm.$^{-1}$. When we consider that the only steric effect that we need to assume is one between a fluorine and a hydrogen atom, the magnitude of the resulting change is surprising. Evidently we must conclude, as we already have in the case of the polyenes, that resonance in the triplet state is extremely sensitive to any steric strain. A still larger effect was found for 2,2′-dichlorobiphenyl, with $\bar{\nu}_P = 25000$ cm.$^{-1}$, which is not far from the value for *p*-dichlorobenzene. Evidently the central double bond is now already completely inhibited, for as we proceed to biphenyl in which all four *ortho* positions are occupied by chlorine ($\bar{\nu}_P = 24500$ cm.$^{-1}$) and to 2,2′,4,4′,6,6′-hexachlorobiphenyl ($\bar{\nu}_P = 23200$ cm.$^{-1}$) we see a falling off in $\bar{\nu}_P$, due simply to chlorine (*cf.* benzene and *p*-dichlorobenzene). It would be hard to fit this steric effect with any other theory of the phosphorescent state than the one that we are presenting.

So far we have treated only cases in which the triplet state is produced by the loss of one double bond between carbon and carbon. We must next consider cases involving the breaking of one member of the carbonyl double bond, as



$$\begin{array}{c} \overset{*}{\text{O}} \\ | \\ \text{H}_3\text{C}-\underset{*}{\text{C}}-\text{CH}_3 \end{array}$$

Numerous attempts to obtain phosphorescence from **acetone** failed. If, with this highly unsymmetrical double bond system we can use the same method of calculation as heretofore, we find from bond energy tables that it would take at least 82 kcal. to break the double bond of a ketone, as compared with the 45 kcal. that we have used for the carbon to carbon double bond. In so small a molecule as acetone we must also have considerable repulsive energy. Even if the value of ρ were one-half or one-third as great as in ethylene, the energy calculated for the triplet state would be much higher than that for the fluorescent state (about 90 kcal.) of acetone. We have already mentioned that under such circumstances phosphorescence is not likely to be observed.

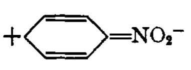
However, the energy of the triplet state appears to be greatly reduced merely by replacing the methyl groups by isopropyl groups; for we were able to obtain the phosphorescence of **di-isopropyl ketone** with $\bar{\nu}_P$ at 25900 cm.$^{-1}$. It is probable that the two branched alkyl groups, by second order resonance, or hyperconjugation, which they are known to exhibit, allow a wider separation of the odd electrons, thus diminishing the value of ρ and also permitting some resonance of the odd electrons in the triplet state.

We shall not at present discuss in detail the data that we have obtained from the numerous aromatic aldehydes and ketones, although it may be noted that E_T is a little less for aldehydes than for corresponding ketones, just as the bond energy is a little less in the former.[36] It is evident from the low values of their triplet state energies that there is a great deal of resonance of the odd electrons in the triplet state, increasing with the complexity of the conjugation, until in **dibenzalacetone** $\bar{\nu}_P$ is only 18500 cm.$^{-1}$, and ΔE_R is negative.

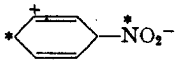
It seemed very important to find the phosphorescence of **thiobenzophenone**. We looked for it in the infra-red but, on account of its very short life, the spectrum was not obtained until the phosphoroscope was dispensed with. Let us see how E_T can be roughly calculated from that of benzophenone. In both compounds ρ of equation (3) is negligible. The normal resonance energy should be about the same for both compounds, and this must certainly be true for resonance in the triplet state; hence ΔE_R should be the same for both. Thus the difference in E_T should be the difference in B. E_T for benzophenone is 73 kcal. The difference in B from Pauling's tables is 33.5 kcal. We thus calculate E_T for thiobenzophenone as 39.5 while our measured value is 43 kcal. The agreement is within the accuracy of the bond energies. We have thus succeeded in calculating the triplet state energy of a new type of molecule from data which would appear irrelevant with any other explanation of the phosphorescent state.

Thiobenzophenone and **biacetyl,** both with extremely short-lived phosphorescence, are of special interest, since we shall show in our next paper that they both exhibit measurable absorption from the singlet to the triplet state, even in non-rigid media; thus proving that the phosphorescent state is not limited to rigid media.

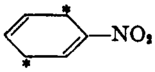
The effect of **auxochromes** may be given a satisfactory qualitative interpretation. A strong acid auxochrome, like the **nitro** group, tends to take on electrons at the expense of an aromatic or other conjugated group to which it is attached. In ordinary resonance of the singlet state it does so by forming a double bond, the extra electron-pair coming from the rest of the molecule, as in the following formula (a) for **nitrobenzene**.



(a)



(b)

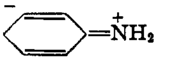


(c)

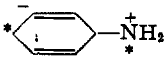
If now we consider the double bond split to give the triplet state, we have some formula such as (b), which also can be derived from the classical formula by considering an electron pair in the aromatic groups uncoupled to give two electrons of parallel spin, one of which is then transferred to the nitro group. The triplet forms corresponding to those of benzene itself (c) probably contribute little to the triplet resonance state, and we can consider that one of the odd electrons is attached permanently to the NO_2 group while the other odd-electron resonates between various positions in the aromatic group.

When we turn to less strongly acid auxochromes such as the **aldehyde, cyanide** and **carboxyl** groups, E_T increases in the given order, and we may suppose that the resonance forms of the type (b) become less important, while those of type (c) become relatively more important.

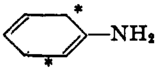
The treatment of basic auxochromes is essentially the same. Here in the case of **aniline** the forms corresponding to (a), (b), and (c) are (d), (e) and (f).



(d)



(e)



(f)

Now when an electron pair is uncoupled, one of the odd electrons may go to the **amino** group, the other remaining on the aromatic group. With such a strong basic auxochrome as NH_2 we may regard the (e) forms as almost solely contributing to the resonance of the triplet state. On the other hand, with a weak basic auxochrome such as **hydroxyl** or **methyl** the importance of the (e) forms diminishes, while that of the (f) form increases.

If we have two auxochromes of opposite types, as in ***p*-nitroaniline** and **1-nitro-5-aminonaphthalene,** the lowering of the energy of the triplet state is greater than that produced by either auxochrome alone. On the other hand, **1-nitro-2-aminonaphthalene** has the same $\bar{\nu}_P$ as **α-nitronaphthalene**. This seems to be a simple "ortho" effect.

With two auxochromes of the same type a peculiar result is obtained. **1,8-Diaminonaphthalene** has, as might be expected, a lower E_T than **α-naphthylamine**. On the other hand, with two nitro groups, as in **1,5-** and **1,8-dinitronaphthalene** and **4,4′-dinitrobiphenyl,** the values of E_T are the same or a little higher than those of the corresponding mono-nitro compounds. It would appear, in these dinitro compounds, that one of the odd electrons may be on one NO_2, or the other, but does not resonate between them.

This suggests some distortion of the molecule such as we have postulated for benzene.

We shall not attempt at present to discuss the triplet state resonance in some of the more complicated molecules. It is evident that in some of the dyes the resonance of the triplet state is very great, and, in **crystal violet** and **eosin,** ΔE_R is negative. The phosphorescence of the color bases is interesting, for in these carbinols the central carbon is, in the ordinary sense, saturated, and might be expected to act as an insulator. That it does not do so is shown by the fact that the carbinols of crystal violet and malachite green have values of $\tilde{\nu}_P$ far below the values that would be obtained for dimethylaniline. This ability to resonate through the central carbon is, however, not confined to the triplet state, for the normal absorption bands of such carbinols lie in the near ultraviolet.

9. **Conclusion and Acknowledgment.**—In the absence of any previous literature on resonance in the triplet state, we have been obliged to feel our way gradually, making numerous hypotheses and testing them by experiment. Perhaps some of our conclusions may have to be modified in the light of further experiment and theory, but we are convinced that the framework is sound, and that the chemical evidence definitely proves that in all the molecules we have studied the phosphorescent state is the triplet state.

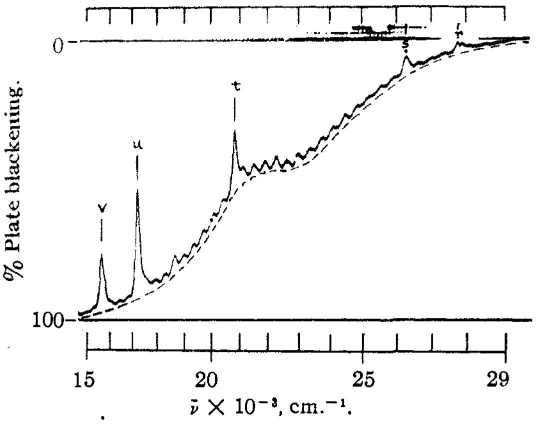


Fig. 6.—Oxygen absorption bands in liquid air.

Phosphorescence has been found, not in every molecule, but in all sorts of molecules, complex or simple, organic or inorganic. We consider that all of the normal and excited states of a molecule fall into two classes of different multiplicity. Ordinarily these are the singlet and triplet classes[43] illustrated in Fig. 1. The lowest member of one class is the stable state; that of the other is a metastable state. While ordinarily the stable state is singlet, in oxygen (also in S_2 and SO) and in the organic biradicals the singlet state is the metastable one.

We are greatly indebted and express our sincere thanks to Professor L. Zechmeister for samples of pure all-*trans* lycopene; to Dr. L. Michaelis for phenazine; to Professor A. L. Henne for hexachlorobutadiene; to Dr. J. D. Heldman for a sample of benzene, purified by fractional distillation; to the Shell Development Company for highly purified butadiene; and to the Forest Products Chemical Company for biacetyl and acetyl propionyl. We are greatly indebted to Professors O. Redlich and H. S. Frank for discussions of the vibrational states, and to Professor G. E. K. Branch for many discussions of the various problems of resonance. Especially we wish to acknowledge our obligation to Professor M. Calvin who not only has maintained a constant and helpful interest in our investigation, but has also had prepared for us under his direction several substances crucial to the testing of our hypotheses, namely, thiobenzophenone, 9,10-diphenylanthracene, *t*-4-nitrostilbene and the various halogen derivatives of biphenyl.

Experimental

Spectroscopic Methods for Studying Phosphorescence.—The methods of observing and measuring phosphorescence spectra are so simple that almost any laboratory has sufficient equipment. It is true that we had available a quartz dewar (inner tube 25 cm. long and of 7 cm. diameter) but many of our early experiments were made in a Pyrex dewar, which, however, has two disadvantages. First, it has a phosphorescence of its own in the orange-red (band X, Plate II, 6), which interfered with the observation of a few of our substances, and, second, it does not transmit the high frequency light required for the excitation of phosphorescence in such a substance as benzene. Liquid air is desirable but not essential since phosphorescence can be readily observed in a bath cooled with solid carbon dioxide (for various rigid solvents see Lewis and Lipkin[3]). Whenever available, liquid nitrogen would be preferable to liquid air because of the pronounced oxygen absorption bands of the latter. These are shown in Fig. 6, which is a tracing of an E. K. III-F plate exposed (dotted line) to a tungsten lamp (No. 2 photoflood), and (solid curve) the same through 7 cm. of fresh liquid air. In addition to the peculiar fine-structure, we see the strong absorptions *r*, 27800 cm.$^{-1}$; *s*, 26200 cm.$^{-1}$; *t*, 20800 cm.$^{-1}$; *u*, 17200 cm.$^{-1}$; *v*, 15700 cm.$^{-1}$.

Our apparatus is shown in Fig. 7. (A) is a G. E. high pressure mercury arc, A-H6, enclosed in a quartz jacket. (L$_1$) is a quartz condensing lens. (F) is a filter of aqueous copper sulfate, used only when the material studied is subject to rapid photo-oxidation. (B) is a light-baffle of blackened cardboard. (P) is a rotating can mounted on a variable speed motor with a maximum of 1800 r. p. m. A section is cut out about a third of the way around the can so that the sample is alternately illuminated and viewed by the spectroscope. The dewar (D) is supported so that it does not touch the can. It contains the liquid air (C), and the quartz sample tube (T) containing the solution to be studied. This is placed as far to the right as possible, partly to increase the apparent intensity, and partly to diminish the absorption of the phosphorescent light by the liquid air. (L$_2$) is another lens which focuses the phosphorescent light upon the slit of the spectroscope.

Some visual observations were made with a simple constant-deviation wave-length spectrometer mounted behind the phosphoroscope (Fig. 7). The spectra were photographed by means of a Hilger Medium Quartz Spectrograph, with a dispersion of 130 cm.$^{-1}$ per mm. at 20000

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[43] We shall not consider here the possibility of a quintuplet state, nor shall we consider the numerous cases of phosphorescence that we have observed in odd-molecules, where presumably the transition is from a quadruplet to a doublet state.

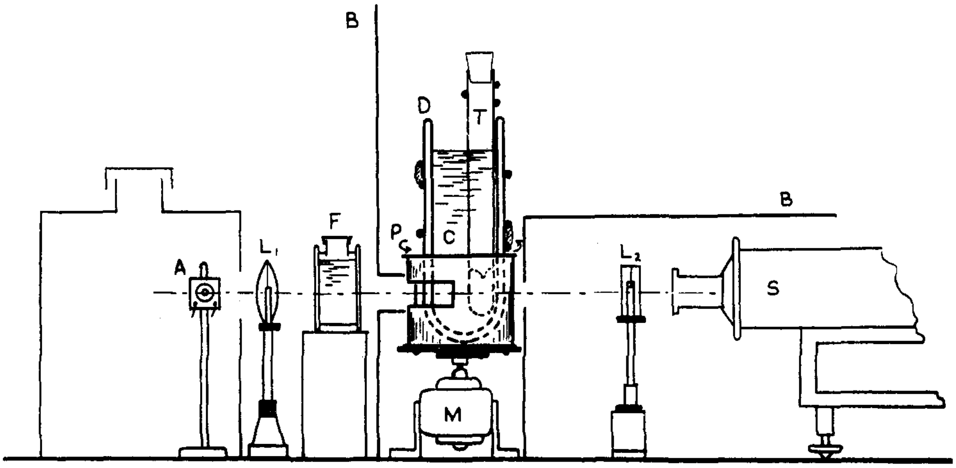

Fig. 7.—Apparatus.

cm.$^{-1}$, using slits of 0.05 mm. to 0.50 mm. (see notes to Plate II for typical exposures). E. K. 103-F Plates were found most suitable for general work, while III-O plates were used for ultraviolet spectra, and ammonia hypersensitized I-L plates were used in the infra-red. The tracings of spectra were made on a Zeiss Recording Microphotometer using tracing slit-widths of usually 0.3 mm., and a scale magnification of 2. The wave-numbers determined by the tracing method are accurate to about 50 cm.$^{-1}$, while the visual observations may be in error by 100 to 200 cm.$^{-1}$ due to errors in estimating the maxima of broad bands.

In cases where fluorescence and phosphorescence were studied simultaneously (Fig. 3) the rotor was discarded and the exciting light fell on the same face that is viewed by the spectroscope. With suitable filters in the primary and secondary beams, none of the primary light reaches the spectroscope. In the one case of thiobenzophenone this method had to be used, since the half-life of phosphorescence is short compared with the time of revolution of the rotor.

When a solution of EPA is placed in liquid air it does not become entirely rigid for ten or twenty minutes, depending on the size of the tube. The process of becoming rigid is presumably analogous to a freezing, in that a good deal of heat is set free. At the same time the surface sucks in to form a deep meniscus. Illumination before rigidity sets in may cause many photochemical processes which are impossible in a state of complete rigidity. Our solvents such as ether, isopentane and alcohol usually used in an EPA mixture (5 ether, 5 isopentane, 2 ethanol, by volume) all ordinarily contain phosphorescent substances, which however may be sufficiently removed by a single distillation with a column of a few theoretical plates. However, the alcohol and ether deteriorate markedly on standing a week or two.

In order to make sure that the change of luminescence observed in the solutions of α-nitronaphthalene, after illumination, was not due to a heating effect, we cooled our solution until it became noticeably viscous. A thin metallic plate was dipped in the solution and then immediately plunged into liquid air. The thin film must remain at the temperature of liquid air. Such films were used in the study of the rate of change of the phosphor as a function of intensity and time of illumination.

Purification of Materials.—Every type of chemical problem has its own criterion of purity. In our present case a substance was considered to be pure when its phosphorescence spectrum remained unchanged upon further purification. In the case of some less important substances, whose spectra seemed unambiguous, the best commercial preparations were used, but for the most part each group of substances presented a new problem of purification. Basic substances, and even slightly basic substances such as benzophenone or anthracene, were purified by fractionally shaking out, between an organic solvent and aqueous sulfuric acid of such concentration that the solute is distributed about equally between the two phases. In this way carbazole was separated from its impurities, even from the weaker base anthracene. In other cases fractional crystallization gives the best results. In the case of naphthalene several recrystallizations from toluene (at about −50°) gave a sample with a clean phosphorescence spectrum. In nearly all cases, and often in addition to the other methods mentioned, a final purification was made by distilling or subliming in a very high vacuum at the appropriate temperature, which varied from well below room temperature to about 80° for the least volatile substances. The liquids were distilled in a wide H-tube with one end dipping in liquid air; the solids, and sometimes the liquids too, were evaporated from an outer tube containing the original material to an inner tube situated just above the material and containing liquid air. In some cases the absorption spectrum (to be discussed in our next paper), as well as the phosphorescence, was used as a criterion of purity. One distillation of nitrobenzene at 15° was sufficient to give a pure absorption spectrum. On the other hand, two sublimations of nitronaphthalene at 40° were necessary. The yellow or brown impurities usually found in such substances, and which after purification reappear on exposure to air, are apparently much less volatile than the parent substances. They usually give an orange phosphorescence. Samples of benzene, even one obtained by careful fractional distillation, showed a spurious phosphorescence, which disappeared during illumination. This effect disappeared when the benzene was fractionally crystallized in the following manner: 500 cc. of the best available benzene was cooled in ice until nearly all frozen. The supernatant liquid was poured off, the benzene melted, and the process repeated several times. We believe that this simple method gives a product of extraordinary purity.

Summary

This paper deals with the phosphorescence frequently observed when a definite chemical species, organic or inorganic, is in homogeneous solution in a transparent, usually rigid, solvent. After a brief discussion of the Jablonski diagram and the reality of the phosphorescent state, it is shown that, in spite of many previous statements to the contrary, each substance has a unique phosphorescent state. Sometimes a substance changes its phosphorescence with continued illumination (Goldstein), but this is due to a new

substance produced by photochemical action (usually photo-oxidation). These photochemical reactions are usually of the first order, but sometimes of the second order, with respect to the photons. The latter reactions are shown to be due to the action of photons on the phosphorescent state itself. The double phosphorescent state found in some dyes is due to the presence of a pseudo-isomer.

The pattern of the phosphorescence bands is so sharp and characteristic that it will serve well for the identification of substances. The whole structure of the phosphorescent band systems is due to the fall from the phosphorescent state to different vibrational excitations of the ground state. The difference between this structure and that of fluorescence is discussed. The fact that some substances show no phosphorescence is interpreted.

The energy of the phosphorescent state (that of the ground state being taken as zero) is calculated from the position of the band of highest frequency. The effect of band width upon this calculation is discussed. This characteristic energy, for eighty-nine substances, is given in Table II.

The structure of the phosphorescence bands is shown to be important in the study of the vibrational levels of the normal molecule, since it brings into prominence vibrations that are often prohibited in infrared and Raman work. Only two of the many spectra are discussed in this regard: β-chloronaphthalene and benzene. In the latter case it is shown how the identification of the band intervals with known vibrations of normal benzene permits conclusions concerning the size and shape of the phosphorescent state—conclusions that are verified in the theoretical section.

The dependence of the energy of the phosphorescent state upon the presence of auxochromes is discussed. It is also shown that the lifetime of the phosphorescent state is greatly affected by certain substituent groups. The phosphorescence of carbon dioxide, sulfur dioxide, and other inorganic substances is mentioned, but further discussion postponed.

Arguments are advanced for the identification of the phosphorescent state with the triplet, or biradical, state of the molecule, and the distinction between fluorescence and phosporescence is defined. The most conclusive evidence that the phosphorescent state is the triplet state is furnished by study of the energy of that state, for a large number of organic molecules. An equation is set up for the energy of the triplet state, as dependent upon the energy required to break a double bond, upon the repulsive energy, and upon the difference in resonance energy between the normal and the triplet states. The data verify the theory. In particular the cases of anthracene, of biphenyl and its ortho derivatives, and of thiobenzophenone afford remarkable confirmation of the theoretical predictions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE IOWA STATE COLLEGE]

On the Nature of the Starch–Iodine Complex[1]

BY R. E. RUNDLE, JOSEPH F. FOSTER AND R. R. BALDWIN

The nature of the interaction between starch and iodine to form the blue starch–iodine complex has interested chemists since 1812, but has never received adequate explanation.[2] Recently the structure of the complex has been made known, and further pertinent facts concerning complex formation have been revealed by the potentiometric[3] and spectrophotometric[4] titrations of starch and its components with iodine. In this paper an attempt is made to explain the nature of the starch–iodine interaction in the light of these new findings.

It has been found that only the amylose (unbranched) component of starch forms a stable blue complex with iodine,[3] so that the major portion of this paper will be devoted to the amylose-iodine complex. The less stable, red complex formed with amylopectin will, however, receive brief attention.

The structure of the amylose–iodine complex has been established, by optical[5] and X-ray[6] investigations, as a helical amylose chain within which the iodine molecules are arranged parallel to the helix axis (Fig. 1). Freudenberg and associates, who, following Hanes,[7] proposed the above structure of the starch–iodine complex, also attempted to explain the interaction of starch with iodine in terms of the structure of the complex.[8]

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(2) For a review of all but the most recent literature on the starch-iodine complex see G. Barger, "Some Application of Organic Chemistry to Biology and Medicine," McGraw-Hill Book Co., Inc., New York, N. Y., 1930, pp. 127–176.

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(5) R. Rundle and R. Baldwin, *ibid.*, **65**, 554 (1943); R. Rundle and D. French, *ibid.*, **65**, 558 (1943).

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(7) C. S. Hanes, *New Phytologist*, **36**, 101, 189 (1937).

(8) K. Freudenberg, E. Schaaf, G. Dumpert and T. Ploetz, *Naturwissenschaften*, **27**, 850 (1939).