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Author

Hirshberg, Yehuda.

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BY BOMBARDMENT WITH ELECTRONS

BERKELEY, CALIFORNIA

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Abstract

The effects of electron irradiation at low temperatures upon a number of bianthrone and spiropyran compounds have been examined. The colors induced have been found to be very similar in properties to those obtained by ultraviolet irradiation of the same compounds.

FORMATION OF REVERSIBLE COLORED MODIFICATIONS
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Yehuda Hirshberg

Radiation Laboratory
University of California
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Introduction

Lewis and Lipkin¹ first reported that some colorless organic compounds produce colored modifications when their rigid-media solutions are irradiated with ultraviolet light. Those colors so produced are stable while the solutions are kept rigid; with the loosening of the rigidity the colors disappear spontaneously.

In 1950 Hirshberg² reported that compounds belonging to the bianthrone series, either thermochromic or nonthermochromic, develop strongly colored species when their solutions are irradiated for a short time with the 365-m μ triplet of a mercury arc at 213°K. When the colored solutions are kept at the temperature at which they were produced they remain stable indefinitely. At higher temperatures the colored forms decay at rates that are temperature-dependent. When the temperature of the colored solution is raised to nearly 273°K the original colorless modification is re-formed. The phenomenon described has been tentatively named "photochromism."

*Department of Chemistry and Radiation Laboratory, University of California, Berkeley, California.

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[§]On leave from the Weizmann Institute of Science, Rehovoth, Israel.

¹G. N. Lewis and D. Lipkin, J. Am. Chem. Soc. 64, 2801 (1942).

²Y. Hirshberg, Compt. rend. 231, 903 (1950).

In subsequent publications details were reported about photochromism and its relation to thermochromism, both in the bianthrone series³ and in the spiropyran series.^{4, 5} It has also been found that some spiropyrans can undergo multiple reversible color changes depending upon the temperature at which the irradiation of their original colorless solutions has been initiated. When irradiation is carried out at about 105°K (in a solvent mixture of methylcyclohexane and petroleum ether) some spiropyrans are first converted into colored modifications of type A. When these modifications are slowly heated to about 123°K, they go over spontaneously into a second colored form, type B, which is also produced when the original colorless solutions are irradiated at 123°K. On further heating, to about 163°K, a spontaneous conversion into a third colored modification, type C, occurs. This modification is identical with the one formed as a result of irradiation of the colorless original form at this same temperature.

Until now, there has been no report on the formation of reversible colored modifications of organic compounds by bombardment with high-energy electrons. This report points out for the first time the possibility of the formation of reversible colored modifications from colorless compounds, either of the bianthrone series or of the spiropyran series, when their solutions, kept at appropriate low temperatures, are subject to electron bombardment. The reversible color produced by this new method has been found in each case studied to be similar to the one formed by ultraviolet irradiation (provided that the solutions are kept the same media conditions for electron bombardment as for irradiation). In the three spiropyrans, V, VI, and VIII, it has been found that when their rigid solutions (at liquid nitrogen temperature) are bombarded by electrons of high energy they give rise to multiple reversible color changes similar to those obtained with ultraviolet irradiation under the same conditions, as described above.

³Y. Hirshberg and E. Fischer, J. Chem. Soc. 629 (1953).

⁴Y. Hirshberg and E. Fischer, J. Chem Phys. 21, 1619 (1953).

⁵Y. Hirshberg and E. Fischer, J. Chem. Soc. 297 and 3129 (1954).

The reversible color changes caused by bombardment with electrons were studied with two nonthermochromic bianthrone (I and II) and with eight spiropyrans, three of which are nonthermochromic. The structures of the compounds used in this study are as shown in Fig. 1.

Experimental Procedure

Solvents. Spectro-grade methylcyclohexane (mch) was used to dissolve each of the spiropyrans studied, and pure-grade isopentane was added to the solutions in proportions of 1:1 by volume. These solvent mixtures always produced a clear transparent rigid glass when cooled down to liquid nitrogen temperature. At temperatures a little higher than 105°K the mixtures formed very mobile clear solutions. Since the bianthrone are insoluble in both solvents listed above, a mixture of reagent-grade toluene and absolute ethanol (1:1) was used as solvent for these compounds. Such a mixture forms a clear transparent rigid glass at all low temperatures below 123°K .

Target cell. Pure all-transparent quartz Dewar-type special cells were used as target cells for each experiment. These cells have four plane parallel polished windows with a light path of about 2 cm and an inner diameter of about 13 mm. A cross section of such a cell is shown in Fig. 2.

Electron Source. A linear accelerator functioning at 3 Mev furnished the high-energy electrons; they hit the target without passing through the electromagnetic monochromatizer, which would produce bending. Before reaching the target solution the electrons had to pass three walls of quartz, each having a thickness of about one millimeter.

Mode of Bombardment. The dewar-type cell containing the target solution was shielded with a lead sheet about 3 mm thick. In the middle of the broader side of the cell, which was at right angles to the plane parallel windows, there was an opening about 3 mm in diameter through which the electrons could reach the target solution (see Fig. 2, T). By this mode of bombardment, the plane parallel polished windows could be kept transparent for spectrophotometric measurements of the color produced during the electron bombardment.

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Fig. 1. Structures of compounds used in study of reversible color changes induced by irradiation.

Fig. 2. Quartz dewar-type vessel for low-temperature spectra.

Spectrophotometric Technique. A special holder was built for the dewar-type cell to permit measurement of the absorption spectra with the aid of the Cary Recording Spectrophotometer, Model 14. The spectra of the original colorless solutions were first recorded, and after the electron bombardment the absorption spectra of the colors formed were followed carefully with change in temperature until the colors disappeared spontaneously.

Temperature Control. The changes in temperature of the solutions were followed by using a copper-constantan thermocouple directly immersed in the solutions. The temperatures were evaluated by a calibrated millivoltmeter.

Materials. The synthesis of all the compounds studied has been described in previous publications.^{3, 4, 5}

Results and Discussion

1. The Bianthrone Series

When a bianthrone I or II is dissolved in a mixture of toluene-ethanol (1:1) in concentrations of 0.5 to 1 milligrams per 10 ml solvent and kept out of light, the solutions remain, for a very long time, slightly yellow-colored, with no absorption in the visible region. Also, when cooled down with dry ice to about 198°K, they do not change their slight yellow color, if kept out of light. When bianthrone I or II is bombarded at this temperature with highly penetrating electrons from the linear accelerator, as described above, after a few seconds of bombardment its solution immediately turns very brilliant dark green. The absorption maximum of the green color of bianthrone I at 198°K is at 6500 Å. The same compound dissolved in toluene-ethanol (2:8) and irradiated at 203°K with the 365-mμ triplet changes to a green-colored reversible modification with an absorption maximum at 6400 Å. (see Fig. 3a). Bianthrone II, when bombarded with electrons under the same conditions as above, develops very quickly a still deeper green color, with an absorption maximum at 7050 Å. The same compound when irradiated with 365 mμ at 198°K changes into a similar deep-green-colored modification with an absorption maximum at 7000 Å. (see Fig. 3b). Green colors formed either

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Fig. 3. (a) Absorption spectra of bianthrone I at 198°K; and (b) absorption spectra of bianthrone II at 203°K.

from bianthrone I or II by electron bombardment remain stable for a very long time if their solutions are kept at 198°K . The colors start to disappear spontaneously when the solutions are heated to over 223°K .

From the results obtained with the two bianthrone, which are nonthermochromic, it seems plausible to assume that there is a parallelism between photochromism and the reversible color changes produced by electron bombardment. The essential difference between the two phenomena lies in the energy transfer to the solute that has to undergo the reversible color changes. In the case of photochromism the ultra-violet light is directly absorbed by the dissolved compound, and therefore the needed excitation energy acts directly on the solute, whereas in electron bombardment the energy needed for the excitation of the dissolved compound comes from the ionized molecules or free radicals of the solvents which are formed by the high-energy electrons which bombard them.

2. The Spiropyran Series

Of the eight spiropyrans studied, three were nonthermochromic; these are compounds III, V, and VI. All the spiropyrans, when dissolved in a nonpolar solvent like methylcyclohexane (mch) or isopentane (isp), or in a mixture of both of them, are colorless transparent solutions even when cooled down to liquid nitrogen temperatures.

When dibenzo-spiropyran (III) is dissolved in concentrations of about 0.4 mg in a 10-ml solution of 5 ml methylcyclohexane (mch) + 5 ml isopentane (isp) and then cooled to 123°K , it starts to absorb only in the near ultraviolet. Upon electron bombardment at this temperature a strong pink-violet color appears. The color has a distinct absorption curve, with maxima at about $5300 \text{ \AA}$ and $4700 \text{ \AA}$ (see Fig. 4a). The color remains stable for a very long time, as long as the solution is kept below 143°K . At higher temperatures the decay of the color is temperature-dependent. When the temperature reaches 243°K the color disappears completely, and only the absorption spectrum of the original colorless solution is apparent.

In di- β -naphtha-spiropyran, compound IV, the following is found: 0.2 mg of IV dissolved in the above-mentioned mixture of mch and isp as described above and cooled down to 123°K absorbs only in the near

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Fig. 4. Absorption spectra of spiropyran III and IV.

ultraviolet and is colorless. Upon electron bombardment at this temperature the solution becomes a strong blue-violet color, with absorption maxima at 6200 Å and at 5800 Å. The color and the absorption maxima are nearly the same as those obtained by irradiating compound IV under the same conditions with ultraviolet light (see Fig. 4b). Also, in this case, the color remains stable if the solution is not heated above 143°K. On heating to higher temperatures the color starts to fade, and disappears completely when the temperature is a little over 193°K.

Compound V, which is nonthermochromic, showed multiple reversible color changes when in solution as a rigid glass during the penetration of high-energy electrons. When the temperature of the solution is about 90°K, electron bombardment induces a bluish-green color. This color has a complex absorption spectrum with four maxima: 7000 Å, 6100 Å, 5600 Å, and 5250 Å. When the temperature is raised to 123°K the former bluish-green color turns dark violet, having one absorption band in the visible region with a maximum at about 5650 Å. The decay of the violet color is temperature-dependent and the color disappears completely, reverting to the original colorless solution, when the temperature exceeds 223°K. The only difference between the multiple reversible color changes in compound V just described and those found when this compound is subjected to ultraviolet irradiation under the same conditions consists of the following: in the latter case, the green color that formed, with absorption maxima at 7200 Å and 6000 Å, changed first into a pink color (with a maximum at 5300 Å) before going over into the violet one. It seems plausible to assume that the bluish-green color formed by electron bombardment, described above, contains in itself the intermediate pink color and already partially overlaps the violet color. This will fairly well explain why the absorption of the bluish-green color also has maxima at 5250 Å and at 5650 Å; the former corresponds to the maximum of the pink color and the latter to the violet one. The absorption spectra of the colors formed by electron bombardment of compound V at two distinct low temperatures are shown in Figs. 5a and 5b.

Benzo-xantho-spiropyran VI, which is also nonthermochromic, when subjected to electron bombardment at about 93°K also undergoes multiple reversible color changes. The first color that appears is dark

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Fig. 5. Absorption spectra of compounds V, VI, VII, VIII at low temperatures after various treatments.

blue, with a broad absorption maximum at 6600 to 6500 Å, and with two additional bands at 5700 and 4800 Å. When the temperature of this dark-blue-colored solution is raised to 123°K it changes into a violet color having two absorption bands with maxima at 5700 Å and 4700 Å. Upon further heating to about 203°K the color disappears quickly, and at 263°K the original colorless solution returns. Also, in this case, there is a parallelism between the color changes just described and those which occur when this spiropyran is subjected to ultraviolet irradiation under the same conditions (compare "c" and "d" in Fig. 5).

When a solution of xantho-β-naphtha-spiropyran, VII, cooled to 123°K, is bombarded with electrons, a pink-violet color appears that remains stable at this temperature and has a distinctive absorption curve with one maximum at 5300 Å. The color and the absorption curve are quite the same as those obtained with solutions of this compound when irradiated with ultraviolet light under the same conditions (compare curves "e" and "f" in Fig. 5).

In the case of N-methyl-acridine-β-naphtha-pyrylospiran, VIII, a solution of 0.1 mg dissolved in 10 ml meh + isp was cooled in the target cell to 123°K and subjected to electron bombardment. The original colorless solution turns pink-violet, which remains stable at this temperature. The absorption spectrum has a broad maximum between 5400 and 5200 Å. When the original colorless solution of VIII is cooled first to about 93°K and is subjected at this temperature to electron bombardment, a dark blue-green solution results. This has a distinctive absorption spectrum with a maximum at 7100 Å. Upon heating to 123°K, the blue-green color changes to violet with an absorption maximum at 5500 Å, and on further heating to 153°K the solution becomes pink-violet with absorption maxima at 5400 and 5200 Å. When the temperature is raised to 193°K, the solution quickly loses the color and slowly reverts to the initial colorless form. Also the multiple reversible color changes just described are in agreement with the results obtained when compound VII is subjected to ultraviolet irradiation under the same temperature conditions (compare curves "g" and "h" in Fig. 5).

The two indolino-spiopyrans IX and X are special cases, as described already in more detailed form in a previous publication.⁶ The colored modifications of those compounds seem to be of more basic character than all the other spiopyrans described until now. Because of their special properties the colored modifications of IX and X are assigned a structure in which the predominant hybrid structure is

It can easily attract a proton to the free negative-charged oxygen and form a salt ion, which was found to be of a yellow color with an absorption maxima at 4800 Å for IX and 4900 Å for X.⁶ When those indolino-spiopyrans were subjected to electron bombardment they formed reddish-yellow to yellow colors with absorption maxima between 4900 and 4750 Å. In neutral solvents like those used in the experiments, the colors formed under the same temperature conditions would have produced, by ultraviolet irradiations, violet-red colors with absorption maxima at 5700 and 5800 Å, respectively. But during electron bombardment part of the solvent is decomposed and there is a formation of several different kinds of radicals as well as of hydrogen, which, in the presence of the oxygen dissolved and contained in the target cell, may form some free acids or protons. These acids or protons may then combine immediately with the colors formed from IX and X, and result in the corresponding yellow-colored salt ion.

⁶Y. Hirshberg, J. Amer. Chem. Soc. 78, 2304(1955).

Acknowledgments

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