Magnetochemical Study of Dianthraquinone and its Thermochromism in the Solid State

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Introduction

Harnik and Schmidt1) analysed the crystal structure of dianthraquinone, and established the fact that steric limitations prevent the molecule from being planar, and the distortions within the molecule are distributed over several bonds. In the first place, with the intention of ascertaining the effect of non-coplanarity of aromatic net plane on the delocalization of π-electrons, we examined the diamagnetic susceptibility of dianthraquinone and compared it with those of some related compounds.

The reversible color change on heating (thermochromism) of a solution of dianthraquinone has been of great interest, since Meyer2) synthesized this compound about fifty years ago. He also reported that this compound turns from lemon yellow to green, if it is heated to about 170°C in the solid state. But in this case, recrystallization or boiling with alcohol was necessary to the perfect recovery of the original color. Grubb and Kistiakowsky3), and Theilacker and his associates4) performed spectroscopic investigations, and concluded that the thermochromism in solution is due to the transition between isomeric forms which are in a thermal equilibrium with each other. The same absorption spectrum was also found by Hirshberg and Fischer5), when a solution was irradiated with ultraviolet light at low temperatures. As to the nature of the colored form, Schönberg proposed a betaine-like structure6) and in the later paper an increase of planarity of the molecule7), while many other investigators3,4,8,9) suggested a biradical or long-life triplet state. Only magnetic measurements will make it possible to decide whether or not the colored excited form represents a biradical. But two reports which have already appeared are unfortunately in disagreement with each other. Nielsen and Fraenkel9) reported that paramagnetic resonance absorption can be detected in the green colored solution and solid specimen heated above 265°C; nevertheless Theilacker10) could not find the anticipated decrease of diamagnetism by the direct susceptibility measurements. Thus, the thermochromic phenomenon in solution has been studied by many investigators, but we have few knowledge of it in the solid state. Considerable differences are found even in the temperature at which color change occurs; the values recorded include 170°C2), 240°C11), and 265°C9). To throw further light on the thermochromism in the solid state, we examined the changes of some properties accompanying the color change on heating of crystalline powder of this compound.

Experimental

Materials.—Anthracene and dianthryl were provided by Mr. T. Handa. They were sublimed in vacuo before being used for measurements. Anthrone was prepared by reduction of commercial anthraquinone with hydrochloric acid and tin, and recrystallized from the mixture of benzene and ligroin12). It was oxidized again to anthraquinone with chromic acid, and a repeatedly sublimed specimen was used for the magnetic measurement. Dianthrone (or dianthronyl) was prepared by oxidation of anthrone with ferric chloride in glacial acetic acid13), and recrystallized from Solvesso-100 which was obtained from Standard Vacuum Oil Co.. It was isomerized to dianthranol by boiling with alcohol containing potassium hydroxide, and repeatedly recrystallized from ethanol, and its pyridine compound was obtained by the recrystallization of dianthrone from pyridine as described by Schönberg and Ismail14). Dianthrone was dissolved in pyridine

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1) E. Harnik and G.M.J. Schmidt, *J. Chem. Soc.*, **1954**, 3295.

2) H. Meyer, *Monatsh. Chem.*, **30**, 165 (1909).

3) W.T. Grubb and G.B. Kistiakowsky, *J. Am. Chem. Soc.*, **72**, 419 (1950).

4) W. Theilacker, G. Kortüm and G. Friedheim, *Ber.*, **83**, 508 (1950).

5) Y. Hirshberg and E. Fischer, *J. Chem. Soc.*, **1953**, 629.

6) A. Schönberg, A. Ismail and W. Asker, ibid., **1946**, 442.

7) A. Schönberg, A. Mustafa and W. Asker, *J. Am. Chem. Soc.*, **76**. 4134 (1954).

8) S.L. Matlow, *J. Chem. Phys.*, **23**, 152 (1955).

9) W.G. Nielsen and G.K. Fraenkel, ibid., **21**, 1619 (1953).

10) W. Theilacker, G. Kortüm and H. Elliehausen, *Z. Naturforsch.*, **9**, 167 (1954).

11) R. Padova, *Ann. chim. phys.*, (8) **19**, 408 (1910).

12) "Organic Syntheses", Coll. Vol., **1** (1948) p. 60.

13) O. Dimroth, *Ber.*, **34**, 219 (1901).

14) A. Schönberg and A. Ismail, *J. Chem. Soc.*, **1944**, 307.

and oxidized with bromine to dianthraquinone[15]; it was recrystallized three times from Solvesso-100.

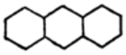
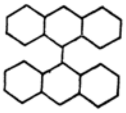
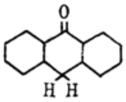
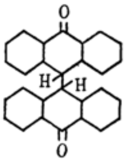
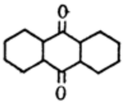
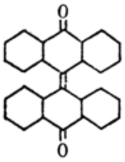
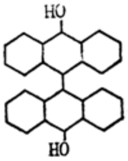
Heat Treatment.—About 1 g. of dianthraquinone which was put in a test tube with a thermometer inserted in it was placed in vacuo and heated by an electric furnace. The temperature of the specimen was measured from time to time, and controlled to ±3°C by means of regulating the applied voltage to the furnace. After the heat treatment, the specimen was cooled down in vacuo as quickly as possible.

Magnetic Measurement.—The susceptibility was measured using a Gouy balance as previously described[16].

X-Ray Measurement.—It was made on a North American Philips recording X-ray diffractometer, using filtered copper radiation.

Table I

Diamagnetic susceptibilities of dianthraquinone and its related compounds

Substance	Formula	Suscept. $(-\chi)$	Molar Suscept. $(-\chi_M)$ obs.	calcd.	lit.
Anthracene		0.731	130	—	129.4[17], 134.2[18]
Dianthryl		0.707	250	254	—
Anthrone		0.609	118	—	125.6[20]
Dianthrone		0.592	229	230	—
Anthraquinone		0.548	114	—	119.6[19], 113[20] 116.9[21]
Dianthraquinone		0.573	220	226	218[20]
Dianthranol		0.679	262	266	—
Dianthranol+2 pyridine	—	0.664	361	363	(pyridine 48.4[22])

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15) E.B. Barnett and M.A. Matthews, ibid., **123**, 380 (1923).

16) H. Akamatu and Y. Matsunaga, This Bulletin, **26**, 364 (1953).

17) P. Pascal, *Bull. soc. chim. France*, **9**, 79 (1911).

18) A. Pacault, ibid., **1949**, D 40.

19) P. Pascal, ibid., **9**, 177 (1911).

20) E. D. Bergmann et al., *J. chim. phys.*, **49**, 474 (1952).

21) S. Banerjee, *Z. Krist.*, **A 100**, 316 (1939).

22) C. M. French, *Trans. Faraday Soc.*, **47**, 1056 (1951).

Results

The diamagnetic susceptibilities of dianthraquinone and the other compounds under consideration are given in Table I[23]. The molar susceptibilities of dianthryl, dianthrone, dianthranol and dianthraquinone have been estimated from measurements on anthracene, anthrone, and anthraquinone respectively with the aid of the Pascal's constants[24], and they also are given in Table I. In these cases, the observed values of molar susceptibility are less diamagnetic than the calculated values except dianthrone the value of which is in agreememt with the calculated one within accuracy of measurements.

The susceptibilities of dianthraquinone heated at various temperatures are given in Table II with the condition of treatment, its color, and the type of X-ray diagram. The sublimed specimen is pale green, but it possesses the identical susceptibility with the original one, and we can not find any difference in the X-ray diagram. On heating to 220°C, its color changes to deep green, susceptibility falls off to some extent, and X-ray diffraction patterns lose sharpness. (Fig. 1, curve B) On further heating to 240°C or above it, diamagnetism decreases still more, and diffraction patterns vanish almost completely (Fig. 1, Curve C). The assignment of indices in Fig. 1, curve A based on the crystallographic constants given by Harnik and Schmidt.

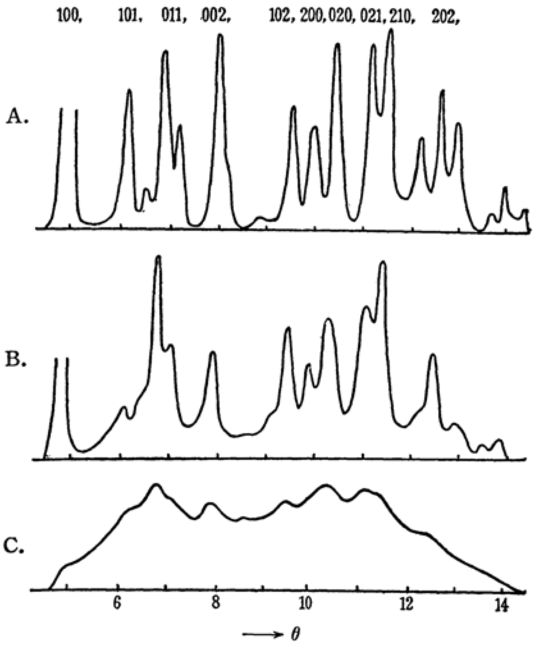

Fig. 1. Change of X-ray diagram of dianthraquinone on heating.
A. Recrystd. B. Heated to 220°C.
C. Heated to 244°C.

TABLE II

CHANGES OF SOME PROPERTIES OF DIANTHRAQUINONE ON HEATING

Conditions	Color	Suscept. $(-\chi)$	X-Ray diagram
recrystd.	yellow	0.573	cryst. (Fig. 1, Curve A)
sublimed (ca. 220°C)	pale green	0.572	cryst.
194°C, 60 min.	yellow	0.570	cryst.
220°C, 60 min.	green	0.538	cryst.+amorph. (Fig. 1, Curve B)
244°C, 60 min.	dark green	0.478	amorph. (Fig. 1, Curve C)
255°C, 80 min.	dark green	0.472	amorph.
266°C, 60 min.	dark green	0.467	amorph.
282°C, 40 min.	dark green	0.446	amorph.
297°C, 60 min.	dark green	0.418	amorph.

Discussion

Diamagnetism of Dianthraquinone.— Aromatic compounds, especially those containing large numbers of rings conjugated or condensed with each other, show the diamagnetic anisotropies which depend strikingly upon the molecular shape[25]. For such cases, it is difficult to estimate the molar susceptibilities by the direct application of the Pascal's additivity law, and we need many constitutive correction constants which are characteristic for each type of condensation of nuclei[26]. In the previous paper[27], we suggested as a compromise to assume that the molar susceptibility of an

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[23] Susceptibility values have been multiplied by 10^6 throughout this paper.

[24] Atomic constants, −2.93 for hydrogen, −4.61 for oxygen in hydroxyl group, and +1.73 for oxygen in carbonyl group. Constitutional correction constants, +5.5 for carbon-carbon double bond and −1.29 for tertiary carbon atom in the position α to hydroxyl group.

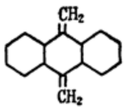
[25] Ref. (16) and references cited there.

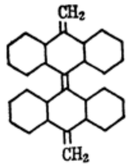
[26] A. Pacault, *Ann. chim.*, (12) 1, 527 (1946). *Rev. sci.*, 86, 38 (1948).

[27] Y. Matsunaga, This Bulletin, 29, 308 (1956).

aromatic compound containing conjugated rings is equal to the sum of those observed for the constitutional fragments of the molecule, and showed that this procedure gives nearly correct values for hydroxyazobenzenes. But in a few cases, the calculated values were also in serious disagreement with the experimental ones, because the effect of conjugation between the fragments of the molecule on the molar susceptibility was left out of consideration. Therefore, our calculated values in Table I by the above-mentioned procedure are nothing but the values for the imaginary cases in which the conjugations between the conjugated nuclei are absent. Then the effect of conjugation will be considered qualitatively with the aid of theoretical results given by London's method. If the theory predicts that conjugation brings about a reduction of diamagnetic anisotropy, our calculated molar susceptibilities will be the upper limits, and if the reverse effect is predicted, they will be the lower limits. McWeeny[28] established the theory that addition of rings, joined to the original system by single links, gives an increase in anisotropy less than that which will be expected in the absence of any conjugation across the bonds, so that dianthryl and dianthranol must belong to the former case. The steric hindrance completely prevents the conjugation between two anthracene nuclei, or their susceptibilities will be less than the calculated values. The observed decrease of diamagnetism suggests the imcomplete prevention of conjugation, although the planar structures of molecules as a whole are not plausible in both cases. As to dianthrone, a new conjugation does not occur by the joining of two anthrones; consequently the agreement between the observed and the calculated susceptibilities is quite natural.

For anthraquinone and dianthraquinone themselves, theoretical investigations have not yet been performed, and it seems that they would be fruitless[29]. For their isoelectronic hydrocarbons, i.e. 9. 10-anthraquinodimethane and dianthraquinodimethane, theoretical values of anisotropies were already presented by Pullman and his associates. Their results are as follows.

anthraquino-dimethane,  $1.941\ \Delta K_{\text{benzene}}$[30]

dianthraquino-dimethane,  $4.033\ \Delta K_{\text{benzene}}$[20]

By analogy, it is plausible to assume that the calculated molar susceptibility for dianthraquinone is the lower limit, as the increase of anisotropy by the conjugation between two nuclei is expected in the reference compound. Theoretically, a similar relation was also predicted for *p*-benzoquinodimethane and *p*-diphenoquinodimethane[30], so that the compound containing two or more ring systems, joined to each other by double bonds, probably gives an anisotropy more than the sum of those of the original systems. Therefore the disagreement between the observed and the calculated susceptibilities for dianthraquinone must be attributed to the other cause. According to the model given by Harnik and Schmidt (Fig. 2), the length of the central ethylene linkage is 1.31 Å., owing to the angle of 40° between the planes of this double bond and the benzene rings, and the absence of the conjugation between the central double bond and four phenyl groups. In such a case, the π-electron system in dianthraquinone may be divided into three parts, namely an isolated central ethylene linkage and two identical conjugated systems. If we substitute the conjugated system of anthrone for each of the latter two, the molar susceptibility—219 will be expected from this model. The magnitude of susceptibility is consistent with the model presented by X-ray analysis. If we assume that the carbonyl groups are also completely localized, owing to the distortions distributed over the conjugated systems, further smaller value for molar susceptibility—212 will be expected. Therefore, it may be concluded that deviations of several degrees from planarity scarcely affect the delocalization of π-electrons.

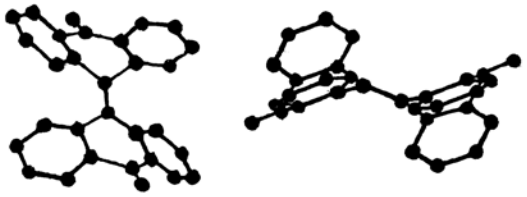


Fig. 2. Perspective view of molecular model (after Harnik and Schmidt).

Thermochromism of Dianthraquinone.— Our results show that the color change from

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28) R. McWeeny, *Proc. Phys. Soc.* A 66, 714 (1953).

29) M.G. Evans, J. de Heer and J. Gergely, ibid., A62, 505 (1949).

30) G. Berthier, M. Mayot and B. Pullman, *J. phys. radium*, 12, 717 (1951).

yellow to dark green is accompanied by the decrease of diamagnetic susceptibility and the complete vanishing of sharp diffraction patterns in the X-ray diagram. This structural change does not occur suddenly at a definite temperature, but takes place gradually at an elevated temperature. The color of a specimen heated to 220°C for one hour was green; however, its change was imcomplete judging from its susceptibility and its X-ray diagram. At 240°C, the change finished within one hour. Hence, the temperature at which we can find the apparent color change must depend on the speed of elevating its temperature. The higher values recorded by Padova[11], and Nielsen and Fraenkel[9] will be due to the rapid heating of the specimen. On the other hand, Meyer's observations[2] cannot be interpreted in the same manner, since we could not succeed in recovering its color by boiling with alcohol, and their recrystallization was practically impossible, as our green specimen was scarcely dissolved in the solvent. We cannot but conclude that Meyer's green specimen is not quite the same as the other authors' including also our own. It is supposed that Meyer said green for the specimen slightly colored, so that the structural change barely occurred in his specimen. This suggestion is supported by his description; namely, he stated that the solution of dianthraquinone turns on heating to deep green and then to blackish green, but for the color of the heated solid specimen, he wrote only green.

Kortüm and his associates[31] discovered that when the deep red sulfuric acid solution of dianthraquinone is added to cold water, dianthraquinone precipitates as a dark green mass for a short period of time, and changes spontaneously to the original yellow form. The solution of the green specimen in concentrated sulfuric acid was also deep red, and we obtained a dark green precipitate similarly, when the solution was poured into water. But in this case, the precipitate did not show such a characteristic color change, and darkened somewhat on standing. For these reasons, the net change occurring in the so-called thermochromism of solid dianthraquinone from yellow to dark green may be concluded as an irreversible chemical reaction, although in its process, the same green form with that which appeared in the reversible thermochromism of solution may be supposed to be an intermediate. The large decrease of diamagnetism accompanying the color change suggests the occurrence of a paramagnetic state, and this expectation is consistent with the result given by Nielsen and Fraenkel, but we cannot discuss further its nature from our measurements.

Summary

The magnetic susceptibilities of dianthraquinone and its seven related compounds were measured by the Gouy method. The effect of conjugation between the constitutional fragments of the molecule was discussed with the aid of theoretical values of diamagnetic anisotropies. The depression of molar susceptibility of dianthraquinone was attributed to the localization of π-electrons in the central ethylene linkage, owing to the large distortion of the molecule. The remarkable decrease of susceptibility and the complete vanishing of sharp diffraction patterns in X-ray diagram accompanying the color change on heating of dianthraquinone were shown. The author concluded that the net change occurring in the so-called thermochromism of solid dianthraquinone is an irreversible chemical reaction.

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[31] G. Kortüm, W. Theilacker, H. Zeininger and H. Elliehausen, *Ber.*, **86**, 294 (1953).