phenylmethane[10] was prepared, and exhibited λ_{max} at 254 mμ (ϵ 24,000) and a shoulder at about 316 mμ (ϵ 150). The difference spectrum between III or IV and I gave λ_{max} 256 mμ (ϵ 20,000) and a shoulder at about 300 mμ (ϵ 4500). The ultraviolet spectrum of p,p'-diacetyldibenzyl gave λ_{max} 222 mμ (ϵ 15,000), 266 (1000), and 273 (900). The difference spectrum between hydrocarbon VII and [2.2]paracyclophane gave λ_{max} 222 mμ (ϵ 14,000), 264 (2000), 273 (10,000), and shoulders at 288 (2400) and at 300 (85). The detailed shapes of the ultraviolet spectra of compounds VII and IXb were very similar, and resembled that of [2.2]paracyclophane except in the 240–280-mμ region. The ultraviolet spectra of 4-carboxy[2.2]paracyclophane and of compounds V and VI very much resembled one another.

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(10) M. H. Duval, *Bull. soc. chim. France*, [4] **7**, 789 (1910).

The Chemistry of 1,2-Bis(p-dimethylaminophenyl)-1,2-diphenylethylene. Molecular Complexes with Iodine[*,1]

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Freshly prepared 1,2-bis(p-dimethylaminophenyl)-1,2-diphenylethylene diiodide contains no water of crystallization and at room temperature undergoes a slow electron transfer between anion and dication to give a yellow-brown solid (IV) with the same composition as the starting compound. This change is rapid at 75° and the final product (IV) is considered to be an n donor complex of iodine and the parent olefin (III). An intermediate in this change shows e.s.r. absorption which is probably due to a Würster-type cation.

In an earlier paper[2] the stability of the monohydrate of tetrakis(p-dimethylaminophenyl)ethylene diiodide (I) was reported. It was pointed out that the removal of water[3] at room temperature resulted in significant changes in the e.s.r., infrared spectra, and color of the solid. The suggestion was made that the loss of water permitted a one-electron transfer to occur with the production of a Würster-type cation which was responsible for the e.s.r. absorption. It was also pointed out that the cold benzene extraction of I, which probably removes water, afforded products which indicated a two-electron transfer between anion and dication.

In the present paper we are concerned with some of the properties of 1,2-bis(p-dimethylaminophenyl)-1,2-diphenylethylene diiodide (II).

Experimental

Materials. 1,2-Bis(p-dimethylaminophenyl)-1,2-diphenylethylene (III).—III was prepared by the method of Buckles and Meinhardt.[4a]

A sample of III was recrystallized for spectral work, from ethanol–chloroform and from ethanol and had m.p. 230–233°.

Certified resublimed reagent grade iodine was used without further treatment. Commercial ethylene chloride was purified according to the careful work of Buckles, *et al.*[4b]

The diperchlorate of III was prepared by the procedure of Wizinger and Fontaine[5] and was recrystallized twice from water.

Anal. Calcd. for $C_{30}H_{30}Cl_2N_2O_8$: Cl, 11.50. Found: Cl, 11.20, 11.20.

Bis(p-dimethylaminophenyl)-1,2-diphenylethylene Diiodide (II).—Potassium iodide dissolved in water was added to a cold aqueous solution of diperchlorate III. The purple-black solid II which separated was collected, washed repeatedly with ice–water, and dried for 24 hr. at room temperature. The diiodide II, unlike I, did not contain water of hydration. Compound II was soluble in water while still wet, but no attempt was made to recrystallize it from water.

Anal. Calcd. for $C_{30}H_{30}I_2N_2$: I, 37.79. Found: I, 37.74, 36.97.

There was no change in weight after heating II for 6 hr. at 75°. The color changed from purple-black through gray to yellow-brown; this heated compound, **IV**, was insoluble in water.

Anal. Calcd. for $C_{30}H_{30}I_2N_2$: I, 37.79. Found: I, 37.00, 36.87.

The purple-black compound II was allowed to stand at room temperature for 1 month. During this time it gradually changed to yellow-brown and there was no loss in weight.

Anal. Calcd. for $C_{30}H_{30}I_2N_2$: I, 37.79. Found: I, 36.98.

The yellow diiodide IV in ethylene chloride treated with copper bronze at room temperature yielded the olefin III.

Instrumentation.—Visible and ultraviolet absorption spectra were determined using a Cary Model 14 recording spectrophotometer. Matched silica cells of path length 1.00 ± 0.01 cm. were used to determine the spectra and 2.5×10^{-5} M concentrations were used for most measurements.

All infrared spectra were obtained using a Perkin-Elmer Model 221 infrared spectrophotometer equipped with double grating.

Electron spin resonance spectra were obtained using a Varian Model 4500 e.s.r. spectrometer fitted with a TE_{102} cavity and a 100-kc. modulation attachment. Ten-milligram samples in 4-mm.-o.d. Pyrex tubes were positioned for maximum signal in the cavity. Estimations of free-radical concentrations were based on comparison with a standard char sample, that had been calibrated in turn against a known amount of diphenylpicrylhydrazyl. Calculations were made by integration of the first derivative of the e.s.r. signals using a planimeter.

Spectroscopic Results

Visible and Ultraviolet Absorption Spectra.—In Figure 1 are shown the spectra in ethylene chloride of 2.5×10^{-5} M solutions of compound III, compound IV, compound II, and the diperchlorate of III.[6] For comparison, the diperchlorate is also shown in aqueous solution. These spectra show that the association of iodine with the olefin III has brought about a small shift in the absorption bands of III at about 282 and 360 mμ, respectively, accompanied by a small increase in the intensity of absorption. Attempts to calculate the equilibrium constant by means of the Benesi–Hildebrand[7] equation were not successful and no absorption

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[*] To Professor Louis F. Fieser.

(1) Reseach Council of Alberta Contribution 284.

(2) R. M. Elofson, D. H. Anderson, H. S. Gutowsky, R. B. Sandin, and K. F. Schulz, *J. Am. Chem. Soc.*, **85**, 2622 (1963).

(3) This reaction was shown to be reversible. It is interesting to note that the dehydration of the diphenylene iodonium derivative of dimedone. $2H_2O$ is reversible and involves a color change from colorless to yellow: J. W. Greidanus, W. J. Rebel, and R. B. Sandin, *ibid.*, **84**, 1504 (1962).

(4) (a) R. E. Buckles and N. A. Meinhardt, *ibid.*, **74**, 1171 (1952); (b) R. E. Buckles, R. E. Erickson, J. D. Snyder, and W. B. Person, *ibid.*, **82**, 2444 (1960).

(5) R. Wizinger and J. Fontaine, *Ber.*, **60**, 1377 (1927).

(6) There is a marked difference between the spectrum of the diperchlorate of III and the diiodide of III. This is due to the fact that the iodide ion is a good donor of electronic charge. Also in the solid state the diperchlorate of III is relatively stable and is therefore unlike the solid diiodide of III which undergoes a gradual change even at room temperature. All these facts are reminiscent of the marked difference between the dinitrate and the diiodide of tetrakis(p-dimethylaminophenyl)ethylene.[1]

(7) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

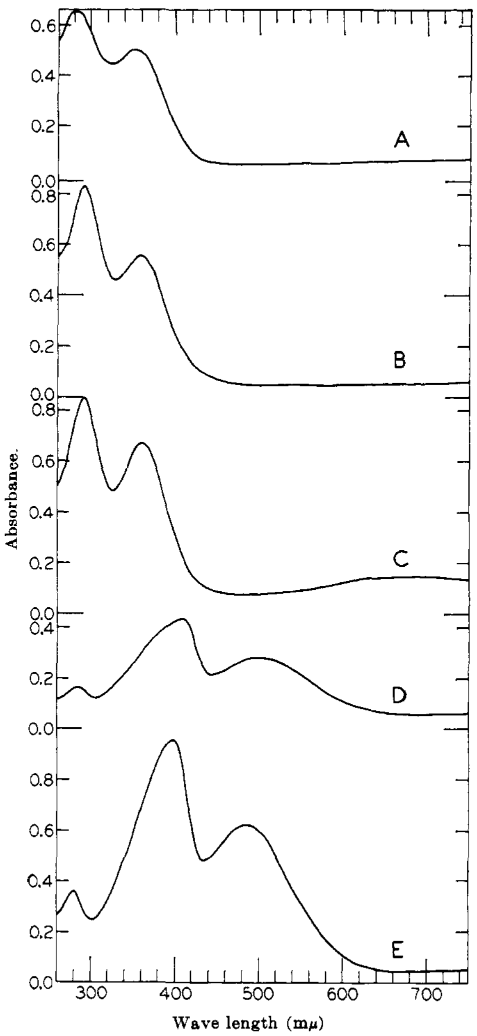

Figure 1.—Absorption spectra: (A) compound III, 2.5 × 10^{-5} M in ethylene chloride; (B) compound IV, 2.5 × 10^{-5} M in ethylene chloride; (C) compound II, 2.5 × 10^{-5} M in ethylene chloride; (D) diperchlorate of III, 2.5 × 10^{-5} M in ethylene chloride; and (E) diperchlorate of III, 2.5 × 10^{-5} M in water.

due to molecular iodine was observed in solutions of II or IV in ethylene chloride. However, small concentrations of iodine of the order of 2.5 × 10^{-6} M might have escaped detection.

Solutions of the purple-black diiodide II in ethylene chloride and solutions of iodine added to III in ethylene chloride show broad weak absorption at about 690 mμ. This latter absorption is not a characteristic of a solution of the yellow-brown diiodide (IV) in ethylene dichloride. The absorption bands of the yellow-brown diiodide are very close to those of the triiodide ion at 295 and 365 mμ in ethylene chloride.[8] The absence of absorption due to a cation seems to rule out the presence of triiodide ion in the yellow-brown diiodide.[9]

Infrared Spectroscopy.—In Figure 2 are shown the infrared absorption spectra in Fluorolube mulls of the olefin III, the yellow-brown diiodide IV, the purple-black diiodide II, and the diperchlorate of III. These spectra show that, while the complex II is quite similar to the olefin III and quite different from the diperchlorate, the yellow-brown complex IV has a pronounced absorption at 1660 cm.$^{-1}$ which is consistent with an isolated double bond.[10] In other respects it resembles the dark complex II and the olefin.

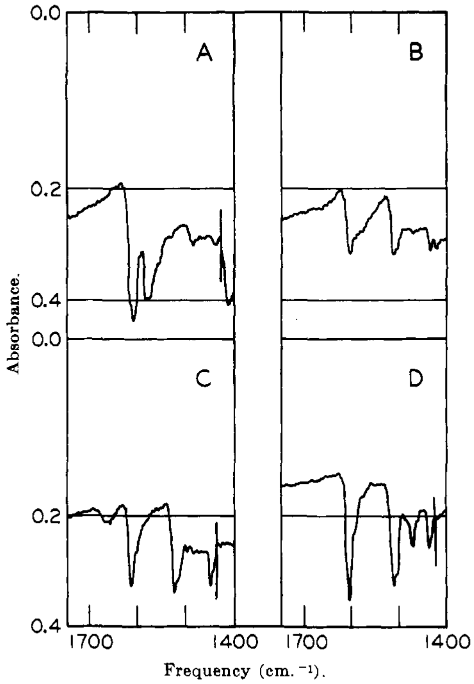

Figure 2.—Infrared spectra of derivatives of 1,2-bis(p-dimethylaminophenyl)-1,2-diphenylethylene in Fluorolube mull: (A) diperchlorate of III, (B) compound II, (C) compound IV, and (D) parent olefin III.

Electron Spin Resonance Spectroscopy.—Freshly prepared bis(p-dimethylaminophenyl)-1,2-diphenylethylene diiodide (II) dried at room temperature gave a relatively strong e.s.r. signal. The width at maximum slope is 14.5 gauss and the g value based on DPPH equal to 2.0036 is 2.0031 ± 0.0001. The strength of the signal corresponded to 1.1 × 10^{19} spins/g showing that about 1.2% of the material was in a free-radical form. As shape and intensity of the signal did not change in measurements made at 77°K. compared with 298°K., the signal definitely does not obey the Curie law in contrast to the signal associated with the diiodide of tetrakis(p-dimethylaminophenyl)ethylene which does obey the Curie law and does broaden at lower temperatures. Evacuation of the sample tube to 10^{-4} mm. at room temperature had no effect on the e.s.r. spectra. The yellow-brown diiodide (IV) prepared by long standing at room temperature or heating for a few hours at 75° showed no e.s.r. absorption. Dark brown samples of II showed absorption of decreased intensity compared to that of purple-black sample II. The diperchlorate of III gave only a very weak e.s.r. signal. The diiodide (II) dissolved in ethylene chloride gave a signal with approximately the same width, 15.5 gauss, as the solids. The solid-free olefin ground with solid iodine afforded a dark brown product which was also paramagnetic.

Discussion

The ultraviolet spectroscopic data show by the displaced absorption peaks that both the purple-black

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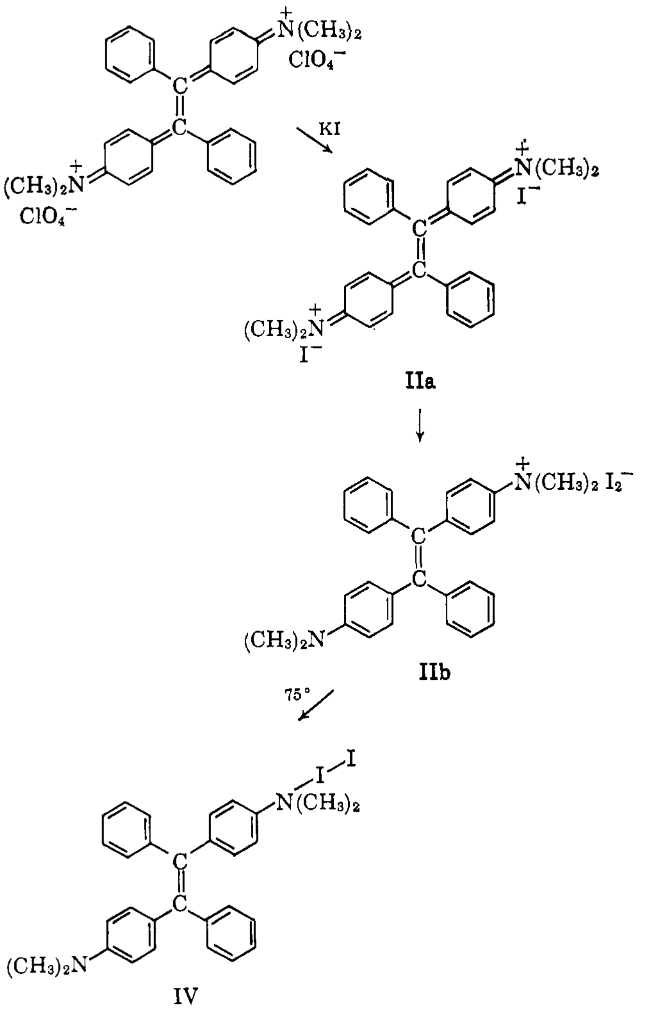
[8] R. E. Buckles, J. P. Yuk, and A. I. Popov, *J. Am. Chem. Soc.*, **74**, 4379 (1952).

[9] It may well be that in solution disproportionation gives rise to a small concentration of triiodide ion associated with a cation. This might be especially true of II where the spectrum of III formed would essentially coincide with that of any triiodide ion present. The long-wave-length absorption could include contributions from a cation associated with the triiodide ion, (We thank the referee for these observations.)

[10] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 31.

Scheme I



diiodide II and the yellow-brown diiodide IV are donor-acceptor complexes of the olefin III with iodine.[11] The infrared and electron spin resonance results and, to a lesser extent, the visible spectra show that these complexes are different. A possible reaction sequence to explain the transformation of the diperchlorate to the purple-black diiodide, II, which gradually becomes lighter in color and forms the yellow-brown diiodide IV, is shown in Scheme I.

Compound II freshly precipitated has considerable water solubility, which it presumably owes to the dication quinoid diiodide form IIa. Gradually as this compound dries at room temperature it becomes less soluble in water, becomes blue-gray in color, and develops an e.s.r. absorption. This is considered as IIb and is depicted as the Würster cation forming a donor-acceptor complex with iodine. The possibility that the e.s.r. signals of such complexes are due to the iodine moiety has been ruled out by the fact that the g value of these complexes is close to that of the free electron, 2.0023.[12] The iodine moiety should give a signal well removed from that of the free electron. For example, the signal assigned to I_2 radicals in KCl crystals doped with KI and irradiated with X-rays has a g of 3.54[13] and has only been observed in crystals. In bulk material or solution orbital interactions apparently broaden such signals beyond detection.

Compound II may be varying proportions of IIa and IIb. However, the diiodide II must have only a transient existence as IIa even in water. As it dried or in ethylene chloride it must exist largely in form IIb or in some related combination of ion pairs. Complex IIb, unlike the e.s.r.-active complex discussed in the previous paper,[1] has some of the properties of aromatic hydrocarbon iodine π-complexes of which the most important is the failure to obey the Curie law. The e.s.r. active complex of tetrakis(p-dimethylaminophenyl)-ethylene diiodide does obey the Curie law and has an increasing width as the temperature is lowered. This means that the complex of the latter resembles the amine quinone complexes while the former resembles the π-complexes of aromatic hydrocarbons with iodine[14] Thus, while both complexes are depicted as Würster cations, the relationship of the iodine moiety must be different. In the case of the tetrakis compound, the original olefin gives up an electron to the iodine to produce the Würster cation with little interaction between the two. In the case of the complex IIb, strong interaction between Würster cation and the iodine moiety is apparent and a π-complex is formed possibly with the iodine in a plane above that of the organic molecule. The yellow-brown complex IV lacks an e.s.r. signal and is analogous to the complexes formed between halogens and tertiary amines. The latter are not paramagnetic[15] and the iodine has been shown by X-ray studies[16] to be located on a line passing through the nitrogen atom of the donor, *viz.* N–X–X with the formation of an essentially covalent bond. Thus the parent olefin (III) acts as an n donor in the yellow-brown complex IV and as a π donor in the darker complex II.

Further confirmation of these views is apparent from the infrared spectra. Thus, complex II in which the iodine forms an ionized π-complex would not have an infrared active olefinic double bond. The formation of a covalent bond between one of the N atoms and the iodine molecule would introduce asymmetry about the double bond which would make this bond infrared active. The location of this vibration at 1660 cm.$^{-1}$ is consistent with an isolated double bond and requires nonplanar structures as far as the relationship of the rings to the olefinic double bond is concerned. The possibility that the yellow-brown solid IV has an iodonium iodide cyclic structure has been ruled out on the basis of spectral and solubility behavior.

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[11] R. Bhattacharya and S. Basu, *Trans. Faraday Soc.*, **54**, 1286 (1958); R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

[12] Y. Matsunaga, *J. Chem. Phys.*, **30**, 855 (1959).

[13] E. Boesman and D. Schoemaker, *ibid.*, **37**, 671 (1962).

[14] M. Bose and M. M. Labes, *J. Am. Chem. Soc.*, **83**, 4505 (1961).

[15] D. D. Eley, H. Inokuchi, and M. R. Willis, *Discussions Faraday Soc.*, **28**, 54 (1959).

[16] O. Hassel, *Mol. Phys.*, **1**, 241 (1958). Also for pertinent references, see (a) C. Reid and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 3869 (1954); (b) S. Nagakura, *ibid.*, **80**, 520 (1958); (c) H. Tsubomura, *ibid.*, **82**, 40 (1960); (d) C. D. Schmulback and D. M. Hart, *ibid.*, **86**, 2347 (1964).