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Some Reactions of Solid Tetrakis-(*p*-dimethylaminophenyl)-ethylene Diiodide Monohydrate¹

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Freshly prepared solid tetrakis-(*p*-dimethylaminophenyl)-ethylene diiodide monohydrate (I) shows very little, if any, free radical activity. Compound I undergoes a reversible room temperature dehydration to produce a solid anhydrous product (III), accompanied by significant changes in the e.s.r., infrared spectra, and color. Compound III exhibits e.s.r. absorption, of Lorentzian shape, which is sensitive to temperature and the presence of oxygen. The heating of III above 75° and the room temperature extraction of I with benzene leads to disproportionation into the parent olefin II and what is probably the diiodide. The e.s.r. of the heated solid IV is similar to that of III except for its insensitivity to oxygen. The complex e.s.r. properties of III and IV are similar to those found in donor-acceptor complexes.

In a previous communication⁶ we reported the preparation of tetrakis-(*p*-dimethylaminophenyl)-ethylene diiodide monohydrate (I) and its optical and e.s.r. spectra in water and in ethylene chloride. Solutions of I in water gave no e.s.r. signal, whereas I in ethylene chloride gave an intense e.s.r. signal. It was suggested that in ethylene chloride an electron transfer occurred to give a cation radical reminiscent of a Würster cation. It was considered reasonable that an equilibrium favoring ionic species in polar solvents should shift in the direction favoring less charged forms in less polar solvents.

The purpose of the present investigation has been to determine the behavior of I in the solid state under varying conditions of temperature, pressure, and humidity.

Experimental

Tetrakis-(*p*-dimethylaminophenyl)-ethylene Diiodide Monohydrate (I).—Potassium iodide dissolved in water was added to an aqueous solution of tetrakis-(*p*-dimethylaminophenyl)-ethylene dinitrate⁶ which had been recrystallized several times from water below 50°. The brilliant green diiodide was air dried at room temperature for 24 hr. and contained one molecule of water which could be removed by heating at 75° in air and which could be absorbed by anhydrous calcium chloride.

Effect of Benzene Extraction.—A weighed sample of I (0.2740 g.) contained in a weighed Gooch crucible was extracted with cold benzene until the weight (0.1484 g.) of black residue was constant (calcd. weight of residue from 0.2740 g. of C₃₄H₄₀N₄I₂·H₂O, 0.1490 g.).

Anal. Calcd. for C₃₄H₄₀N₄I₂ (black residue): I, 60.19. Found: I (Carius), 59.38.

The benzene extract was concentrated to dryness and afforded tetrakis-(*p*-dimethylaminophenyl)-ethylene (II).

Effect of Drying under Vacuum and over Phosphorus Pentoxide.—A weighed sample of I (0.6610 g.) was placed in a vacuum desiccator over phosphorus pentoxide. The pressure was reduced to 5 mm. and after 24 hr. the loss in weight, which was constant, was 0.0166 g. *Anal.* Calcd. for C₃₄H₄₀N₄I₂·H₂O: H₂O, 2.33. Found: H₂O, 2.51. The dried compound was exposed to the laboratory air for 24 hr. until the weight (0.6604 g.) was constant. The reversible dehydration-hydration reaction could be repeated a number of times without any appreciable variation in water content. It was found that standing over phosphorus pentoxide for 24 to 48 hr. at atmospheric pressure would accomplish the dehydration, which could be reversed by exposure to the laboratory air.

Effect of Heating at 75° in Air.—Compound I (0.3728 g.) was dried in air at 75° until the weight was constant. *Anal.* Calcd. for C₃₄H₄₀N₄I₂·H₂O: H₂O, 2.33. Found: H₂O, 2.52. The air-

dried material was extracted with cold benzene and afforded a black residue (0.2108 g.); calcd. wt. of residue is 0.2027 g. *Anal.* Calcd. for C₃₄H₄₀N₄I₂: I, 60.19. Found: I (Carius), 58.74. The benzene extract afforded II.

Electron Spin Resonance Measurements.—Measurements were made with a Varian Model 4500 e.p.r. spectrometer fitted with a TE 102 100 kc. cavity and a 100 kc. modulation attachment; 10-mg. samples in 4-mm. o.d. tubes were positioned for maximum signal in the cavity. Width measurements were based on the vanadyl deuterioporphyrin in benzene.⁷ Estimates of free radical content were based on measurements with 0.25-mg. samples of DPPH dispersed in starch estimated to contain 3.33 × 10¹⁷ free radicals (90% free radical content). Estimates were based on the assumption that the absorption curves were Lorentzian in shape because of exchange narrowing and calculated from the relationship $n = h(\Delta H)^2$ where h is the amplitude of the first derivative at the point of maximum slope and ΔH is the width at the point of maximum slope. Since this assumption could not be valid for the very wide signals observed on the admission of oxygen, the latter results were calculated by integrations using a planimeter. Measurements based on DPPH equal to 2.0023 revealed that all the compounds had g -values in the range 2.0030 ± 0.0003.

Spectroscopic Results

Infrared Spectroscopy.—In Fig. 1 are reproduced spectra in Fluorolube mulls of the dinitrate, the green diiodide monohydrate I, the evacuated diiodide III, the heated diiodide IV, the diiodide, and the parent olefin II in the region 1700–1400 cm.⁻¹. These spectra show that the dinitrate and the diiodide have no benzenoid⁸ absorption at 1520 cm.⁻¹ and they can therefore be considered to be essentially quinoid compounds with intense absorption at 1600 cm.⁻¹. The green hydrate I shows very little if any absorption at 1520 cm.⁻¹ and must also be in the quinoid form. The evacuated diiodide shows a small absorption at 1520 cm.⁻¹ indicating some benzenoid character. The spectra of the heated diiodide shows a much stronger absorption at this frequency indicative of a substantial aromatic content; *cf.* spectrum of olefin in Fig. 1.

Electron Spin Resonance Spectra.—In Table I some e.s.r. measurements on the complexes of tetrakis-(*p*-dimethylaminophenyl)-ethylene with iodine are reported. Freshly prepared I dried at room temperature in air has a very small free radical content as measured by e.s.r. and must be largely in the quinoid form in which the resulting ionic forms are stabilized by the water of hydration. Compound I (10 mg.) placed in 4-mm. o.d. Pyrex tubes and submitted to evacuation underwent a rapid loss of water and change of color from bright green to dark violet with a concomitant increase in free radical concentration. After final evacuation for 2 hr. to 10⁻⁴ to 10⁻⁵ mm. at room temperature the signal reached a limiting value corre-

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sponding to about 4.0×10^{19} spins/g. based on DPPH, or 5% free radical content. When this evacuated material (III) was exposed to an atmosphere of 25 mm. water vapor at 30° for 1 hr. and sealed, the original green color was regained and the free radical content was comparable to that of I.

The same evacuated material exposed to one atmosphere of O_2 for 1 hr. and then sealed showed no visual change but did show a profound series of changes in its e.s.r. behavior. Samples examined within a few hours of admission of oxygen showed pronounced spin broadening due to physical absorption of oxygen molecules. Over a longer period of time (1 month), however, the shape of the absorption curve changed and the material gave a signal which was only 2 to 3 times as broad as that of the evacuated material. On the other hand, admission of nitrogen to the evacuated material produced only a slight decrease in signal intensity.

Compound I heated at 75° in air produced IV which was black and showed an e.s.r. signal corresponding to 4.4×10^{19} spins/g. comparable in width to that of III. The signal from IV was independent of the presence of oxygen and decreased only very slowly when exposed to an atmosphere of 97% humidity over a long period of time, and it showed no appearance of green color. The residue of the benzene extraction, the ditriiodide, had no e.s.r. absorption.

The e.s.r. spectra of III and IV were compared at $298^\circ K.$ and at $78^\circ K.$ While the signals were found to be about three times as wide at the lower temperature the signal intensities obeyed the Curie-Weiss law. The line width continues to increase down to liquid helium temperatures. This behavior accords with that of the aromatic amine-quinone complexes in which the signal width increases with decrease in temperature.⁹

Attempts were made to evacuate single crystals of I in order to detect zero field splittings of a triplet state¹⁰ but without success. Attempts to detect $\Delta M \pm 2$ transitions in bulk crystals of III were not successful.

TABLE I

E.S.R. PROPERTIES OF COMPLEXES OF TETRAKIS-(*p*-DIMETHYLAMINOPHENYL)-ETHYLENE WITH IODINE

Complex	$(\Delta H)^2$, gauss ²	Concn., spins/g.
Monohydrate I (green)	3.02	6.2×10^{15}
Monohydrate I dried in desiccator over P_2O_5	5.38	3.5×10^{15}
Monohydrate I, evac. 10^{-4} mm. (III)	2.71	4.0×10^{19}
III + O_2 after 12 hr.	259	1.3×10^{19}
III + O_2 after 1 month	8.35	1.1×10^{19}
III + N_2	3.20	3.3×10^{19}
III + H_2O , 20 mm. (green)	3.74	1.6×10^{15}
I heated 75° in air	3.20	4.4×10^{19}
I heated 75° in air, humidified 6 wk.	3.24	1.25×10^{19}
DPPH	3.74	1.33×10^{21}

Discussion

The effect of cold benzene extraction of I suggests a mechanism which involves removal of water, which in turn permits a two-electron transfer to occur between anion and dication. The following reaction sequence is quite probable. The weight of benzene-insoluble black residue and the iodine content of the residue indicates

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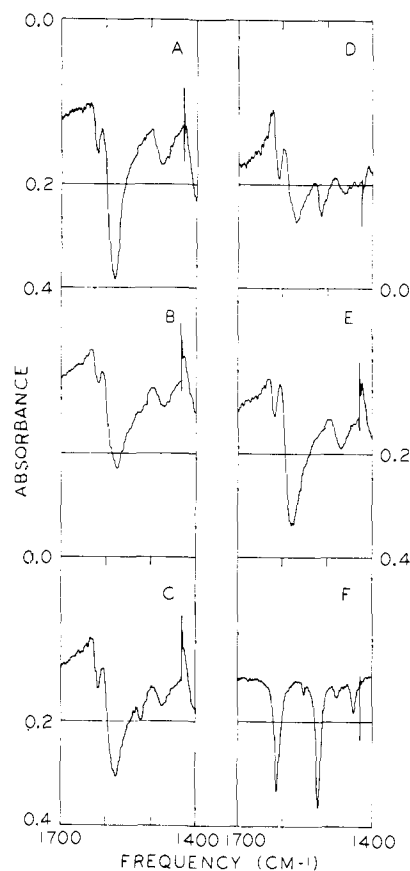
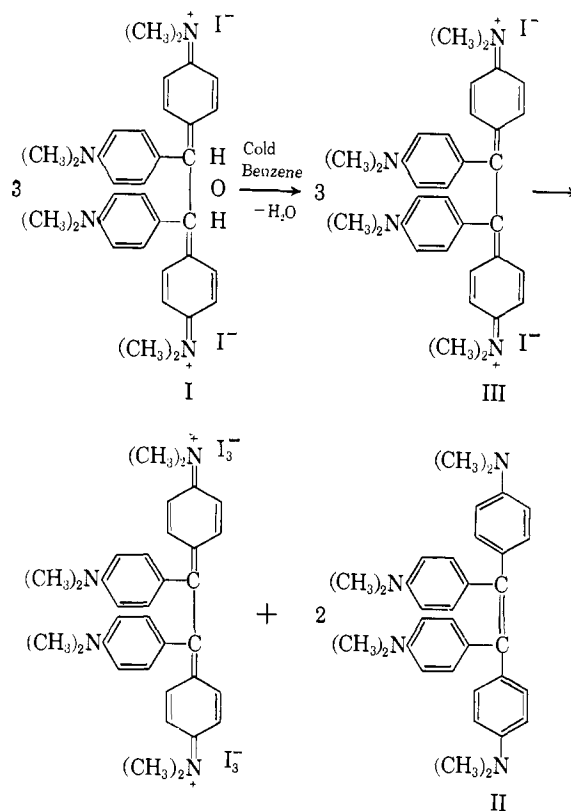
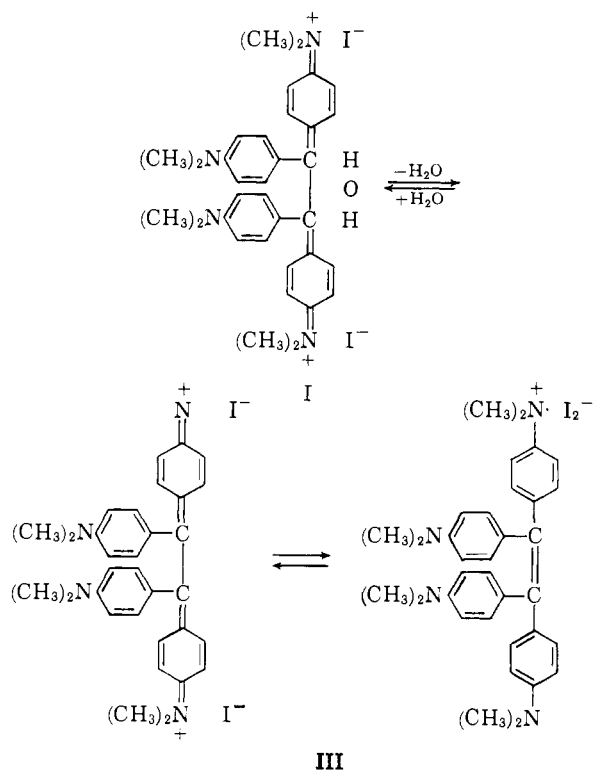


Fig. 1.—Infrared spectra of derivatives of tetrakis-(*p*-dimethylaminophenyl)-ethylene in Fluorolube null: (A) dinitrate, (B) diiodide monohydrate I, (C) evac. diiodide III, (D) heated diiodide IV, (E) ditriiodide, (F) parent olefin II.

that diiodide I is changed to ditriiodide. Olefin is removed by benzene to make the reactions irreversible.





It is quite probable that the effect of drying at 75° is to bring about a reaction sequence similar to the above. In this case olefin and diiodide are both found in the black reaction product.

Drying by evacuation at room temperature to 10⁻⁴ mm. and over phosphorus pentoxide follows a course of reaction which probably involves a pathway which is a one-electron transfer and which is reversible. It may be that this pathway also occurs in the benzene extraction and the 75° drying of I.

At present the nature of the free radicals formed by dehydrating and heating I is not clear. However, the fact that the line width decreases with increasing temperature and that the radical content remains constant as a function of temperature suggests that the radicals may be due to a type of donor-acceptor complex formation.⁹ In the case of III the complex involves iodide, as shown in the reaction just postulated. In the case of IV, obtained by heating I, the complex probably involves triiodide. The connection between the nature of these species and the temperature dependence of the e.s.r. absorption is not apparent.

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Studies in Magnetic Nonequivalence. N.m.r. Spectra of Two-Spin and Two-Spin-Group Systems

BY E. I. SNYDER

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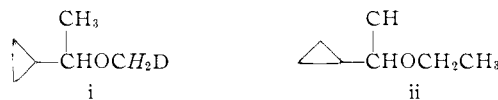
Nuclear magnetic resonance spectra have been obtained for several simple spectral systems whose methylene groups contain magnetically nonequivalent hydrogens, or whose isopropyl groups contain nonequivalent methyl hydrogens. The variation of the chemical shift between nonequivalent hydrogens of saturated systems varies with solvent in the same way as does the chemical shift between the terminal methylenes of the corresponding olefins. This behavior is interpreted as demonstrating the insufficiency of the chemical shift *per se* as a reliable measure of conformational equilibria. Also presented are data which demonstrate a small, but real, solvent dependence of geminal coupling constants.

Introduction

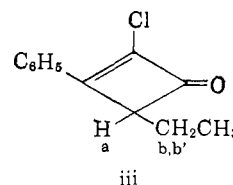
It is known that in systems of the type A-CX₂-B, where A is an atom or group of atoms and B is a group which lacks a plane of symmetry, the X nuclei are sometimes magnetically nonequivalent. This phenomenon has been observed for the methylene hydrogens in the ethyl group of esters,¹ sulfites,² sulfoxides,^{3,4} diethyl sulfide-borane,⁵ diethylmethylammonium iodide,⁶ a thiophosphonate,⁵ carboxylic esters,⁶ for the methylene hydrogens of variously substituted 1,1,1,2-tetrasubstituted ethanes,^{1,7} in the difluoromethylene group of appropriately substituted ethanes,^{1,8-10} and for the methyls of various systems containing an isopropyl skeleton.¹¹ The origin of such nonequivalence has

usually been ascribed to differences in conformer population.^{8,12} However, Waugh and Cotton have explicitly mentioned⁴ that a symmetry argument alone, completely independent of any facets of conformational isomerism, could equally well account for such nonequivalence, although some have not seemed to take cognizance of this latter alternative.

Recently Roberts and co-workers¹³ have interpreted both the lack of nonequivalence in the deuteriomethyl group of i (*vs.* the observed nonequivalence in the ethyl



analog ii) and the inequality of vicinal couplings J_{ab} , $J_{ab'}$ between the nonequivalent methylene hydrogens and



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