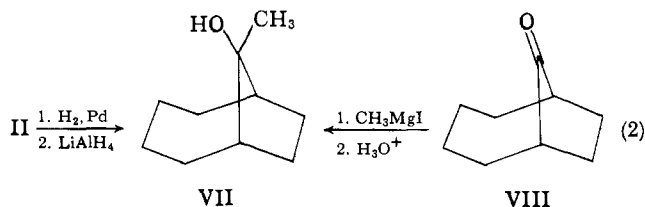


the carbonyl group of VIII nearest the two-carbon bridge is less hindered than from the side facing the four-carbon bridge.



The acyclic tetraene (V) is an air-sensitive yellow solid, m.p. 106–107°. Its structure was established upon its hydrogenation over Adams catalyst to dodecane-2,11-dione (IX) and comparison with an authentic sample. Tetraene V is probably formed by ring-opening of IV; disubstituted 1,3,5-cyclooctatrienes and bicyclo[4.2.0]octadienes isomerize to fully conjugated noncyclic tetraenes.⁹

The structure of VI,³ m.p. 53.5–54°, was assigned as a bicyclo[6.1.0]nonatriene rather than as a stereoisomer of II, IV, or V because of its n.m.r.^{10a} and spectral^{10b} properties and its hydrogenation to 9-acetoxy-9-methylbicyclo[6.1.0]nonane (X).³ Synthesis of X was effected by reaction of the Δ^2 -pyrazoline from 1-acetylcyclooctene with lead tetraacetate to give the 3-acetoxy- Δ^1 -pyrazoline which on pyrolysis yielded a mixture from which X¹¹ was isolated by gas chromatography. The X prepared had retention times and infrared absorption identical with those of the hydrogenation product of VI. It is believed that the ring fusion in VI is *cis* since there is greater strain involved in fusing a cyclopropyl ring *trans* to a relatively rigid cyclooctatriene. The stereochemistry of the 9-acetoxy group as *syn* to the cyclooctatriene ring is implied on the basis of steric factors involved in reaction mechanism (eq. 1).

Cyclooctatetraene dianion (I) has been acylated with other halides. Benzoyl chloride and I give 9-benzoyloxy-9-phenylbicyclo[4.2.1]nonatriene (XII, 62%) and 1,8-dibenzoyl-1,3,5,7-octatetraene (XIII, 7%) along with amorphous hygroscopic material (20%).¹² The melting point (124–125°) of XII¹³ corresponds to that reported^{2a} for dibenzoylcyclooctatriene. Its structure and apparent stereochemistry (the 9-phenyl group is *syn* to the two-carbon bridge) were determined by hydrogenation to 9-benzoyloxy-9-phenylbicyclo[4.2.1]nonane³ (XIV, m.p. 119–120°) which was converted by lithium aluminum hydride to 9-phenylbicyclo[4.2.1]nonan-9-ol³ (XV, 59–59.5°), identical with that prepared from VIII and phenylmagnesium bromide. The identity of XIII³ (yellow needles, m.p. 172–173°, λ_{max} 378 m μ (ϵ 47,000))¹⁴ was confirmed by its hydrogenation to

(8) Ultraviolet absorption: $\lambda_{\text{max}}^{\text{MeOH}}$ 343 (49,500) and 221 m μ (ϵ 4100); infrared absorption: 5.94 m μ (conjugated carbonyl).

(9) A. C. Cope and D. J. Marshall, *J. Am. Chem. Soc.*, **75**, 3208 (1953); R. Anet, *Tetrahedron Letters*, 720 (1961); H. Höver, *ibid.*, 256 (1962).

(10) (a) The n.m.r. spectrum of VI includes a multiplet of relative area 2 at 8.24 τ attributable only to the bridgehead protons. The high field position indicates that the hydrogens are of the cyclopropyl type. (b) Ultraviolet absorption: $\lambda_{\text{max}}^{\text{MeOH}}$ 247 m μ (ϵ 4100); infrared absorption: 5.76 and 8.02 μ (ester group). The ultraviolet absorption of VI at a relatively short wave length (1,3,5-cyclooctatrienes usually absorb at \sim 260–265 m μ) may arise from twisting of the triene chromophore because of the steric requirements of a *syn*-9-acetoxy group or from electronic interaction of these groups (Cf. D. D. Phillips, *J. Am. Chem. Soc.*, **77**, 5179 (1955)).

(11) The synthesis is an extension of the elegant method of J. P. Freeman, *J. Org. Chem.*, **28**, 885 (1963).

(12) Analogous products were obtained from I and *p*-bromobenzoyl chloride.

(13) Ultraviolet absorption: $\lambda_{\text{max}}^{\text{MeOH}}$ 266 (2900), 258 (3050), and 224 m μ (ϵ 11,900); infrared absorption: 5.83 and 7.78 μ (ester group).

(14) (a) Upon heating above its melting point, XIII was converted to an isomer, m.p. 199–200°, λ_{max} 385 (66,000) and 370 m μ (ϵ 89,000). From a comparison of the ultraviolet spectra of the isomers with those of the stereoisomeric diphenyloctatetraenes^{14b} it seems likely that the 173° isomer has one

1,10-diphenyl-1,10-decanedione identical with an authentic sample.¹⁵

or more *cis* double bonds and that the stable isomer, m.p. 199°, has the all-*trans* configuration. (b) L. Zechmeister and J. H. Pinckard, *J. Am. Chem. Soc.*, **76**, 4144 (1954).

(15) V. Auger, *Ann. Chim.*, [6] **22**, 363 (1891).

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A New Assignment of the Polarization of the Charge-Transfer Transition in Crystalline Quinhydrone¹

Sir:

For highly absorbing crystals, specular reflection yields the same type of information that one often obtains from single crystal absorption studies.² Reflection spectroscopy has the advantage, however, that it allows the study of crystals of such high optical density that absorption measurements are extremely difficult and highly unreliable. We have, therefore, as part of a general investigation of the optical properties of a series of donor-acceptor complexes, determined the polarized specular reflection spectra of crystalline quinhydrone from 2000 to 12,000 Å. and report here the room temperature measurements in the 4000–8000-Å. region. These results indicate that in the crystal the charge-transfer transition, which is often taken as a prototype for the whole class of aromatic charge-transfer transitions, is polarized differently than has heretofore been thought.

The reflection and absorption spectra on which this communication is based were obtained on a double-beam microspectrophotometer developed in these laboratories.³ As indicated in Fig. 1, the quinhydrone crystals, which were most satisfactorily grown at an agar-water interface, were flat and elongated with hexagonal cross-section, corresponding to those previously described.^{4,5}

Figure 2 shows the reflection spectra obtained on the prominent (001) face with polarized light whose electric vector is in one case parallel to, and in the other perpendicular to, the needle axis, *a*. Other spectra obtained on one of the four side faces show essentially the same dichroism. In interpreting these spectra one must recall that specular reflection curves generally show "anomalous dispersion" and decrease to a definite minimum before increasing to a maximum as one passes through an absorption band from the high-energy side.⁶ Figure 2, taken in conjunction with the work on the smaller face, thus leads one to conclude that the charge-transfer band is polarized exclusively along the needle axis, or along the molecular columns in the crystal. This result in turn implies that the transition moment is not, as is commonly believed, perpendicular to the rings, but rather lies along a line joining the ring centers, as is illustrated in Fig. 1 for a pair of typically oriented molecules. Were the transition moment perpendicular to the rings, the projections of the transition moments would be such that one would expect a ratio of the integrated charge transfer

(1) The partial support of this work by a grant from the National Science Foundation is gratefully acknowledged.

(2) B. G. Anex, Thesis, University of Washington, 1959; B. G. Anex and W. T. Simpson, *Rev. Mod. Phys.*, **32**, 466 (1960); G. N. Ramachandran and S. Ramaseshan in "Handbuch der Physik," 25-1, Springer-Verlag, Berlin-Göttingen-Heidelberg, 1961, pp. 117–121.

(3) B. G. Anex and L. J. Parkhurst, in preparation.

(4) H. Matsuda, K. Osaki, and I. Nitta, *Bull. Chem. Soc. Japan*, **31**, 611 (1958).

(5) K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 1739 (1952).

(6) R. W. Dichtburn, "Light," Interscience Publishers, Inc., New York, N. Y., 1952, pp. 420–464.

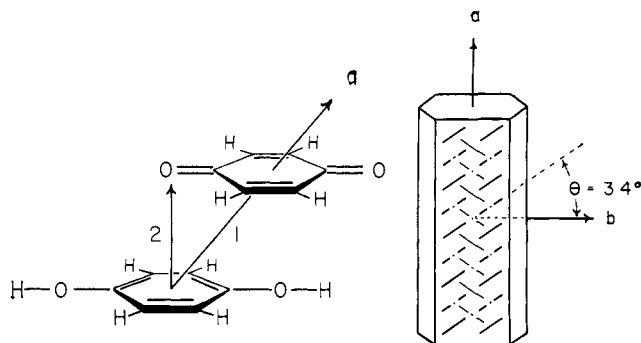


Fig. 1.—Left: The new (1) and former⁵ (2) polarization assignments for the charge-transfer band in crystalline quinhydrone relative to a pair of typical molecules selected from one of the molecular columns in the crystal. Right: Typical morphology of and molecular orientation in a quinhydrone crystal^{4,5}; — · —, benzoquinone; —, hydroquinone. The center column is displaced one quarter unit cell length along c from the two outer columns, c being within a degree of perpendicular to the (001) face.

intensity on a to that on b of 2.2 to 1, a distribution that would certainly lead to structure in the b reflection curve instead of the gradual rise seen in Fig. 2.

The clear disagreement between our results and those generally accepted⁵ and quoted in numerous papers and reviews⁷ prompted us to verify the new assignment through microscopic absorption measurements. These studies have demonstrated that in such work improper alignment or illumination of highly dichroic crystals can easily result in one's obtaining a spurious transmission spectrum for a completely opaque principal direction.³ We have examined very thin single crystals and extremely small, highly dichroic crystals deposited on a microscope slide by slow evaporation of a methanol solution. The former were still completely opaque along the needle axis but did show a band somewhat similar to that reported previously along the b direction,⁵ while the latter permitted measurements throughout the charge-transfer region in the a direction, but were so thin that no b absorption was observed. From these studies it was possible to estimate that the lower limit of the ratio of the integrated intensities from 3600 to 8000 Å. is 30:1 in favor of the needle axis on the (001) face. The b absorption is strongly shifted to higher energies relative to that of a , and may well be related to the $n \rightarrow \pi^*$ absorption found in benzoquinone crystals in the 4500-Å. region⁸ rather than to a weak component of the charge-transfer band.

The fact that the charge-transfer band is polarized in a direction between the centers of the six-membered rings, and not perpendicular thereto, is not in conflict with the theory of charge transfer developed by Mulliken⁹ and actually appears to be more in harmony with it than the former assignment. Mulliken obtained¹⁰

$$\bar{\mu} = ea^*b(\bar{r}_B - \bar{r}_A) + (aa^* - bb^*)eS(\bar{r}_B - \bar{r}_{AB})$$

The first term is simply a vector pointing in the direction

(7) (a) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin-Göttingen-Heidelberg, 1961, pp. 72, 175, 179; (b) S. P. McGlynn, *Chem. Rev.*, **58**, 1113 (1958); (c) S. P. McGlynn, *Radiation Res. Suppl.*, **2**, 300 (1960); (d) S. F. Mason, *Quart. Rev.* (London), **15**, 287 (1961); (e) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952); (f) J. N. Murrell, *Quart. Rev.* (London), **15**, 191 (1961); (g) L. E. Orgel, *ibid.*, **8**, 422 (1954); (h) A. Szent-Györgyi, "Introduction to a Submolecular Biology," Academic Press, New York, N. Y., 1960, p. 76. In addition to the pages noted in (a) and (h), see especially p. 1135 of (b), p. 309 of (c), p. 362 of (d), p. 806 of (e), p. 197 of (f), and p. 441 of (g).

(8) J. C. D. Brand and T. H. Goodwin, *Trans. Faraday Soc.*, **53**, 295 (1957); J. W. Sidman, *J. Am. Chem. Soc.*, **78**, 2363 (1956).

(9) R. S. Mulliken, *ibid.*, **74**, 811 (1952).

(10) R. S. Mulliken, *ibid.*, **74**, 814 (1952), eq. 20.

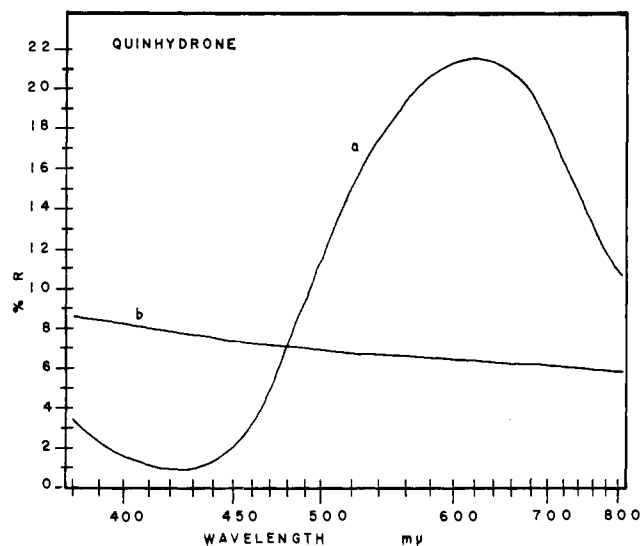


Fig. 2.—Reflection spectra obtained on the (001) face of quinhydrone. a: Light polarized with its electric vector parallel to a ; b: Light polarized with its electric vector parallel to b . The abscissa is linear in energy.

of the dipole moment developed by the charge transfer, or between the centers of the molecules if one considers an isolated donor-acceptor pair as shown in Fig. 1. The second term can, in general, give a component in the plane of the molecules as well as one along the ring centers, but reasonable assumptions concerning the nature of the donor and acceptor orbitals lead to the conclusion that the "in plane" component is small for quinhydrone. The polarization of the crystal transition is thus that which one would predict for an isolated properly oriented 1-1 complex.

Complexes related to quinhydrone have been found to show dichroism similar to that noted here. This work will be reported in forthcoming publications which will also present a detailed accounting of the quinhydrone studies, both experimental and theoretical, and work in progress on the components of quinhydrone.

(11) National Science Foundation Predoctoral Fellow 1959-1962.

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The Structure of *sym*-Triphenylcyclopropenium Perchlorate

Sir:

According to the $(4n + 2)\pi$ -electron rule of aromatic stability, the cyclopropenyl cation is expected to be stable, but thus far, this species has not been isolated. The first preparation of its derivative, *sym*-triphenylcyclopropenyl cation (TPP⁺), was achieved by Breslow and co-workers.¹ Since then, the preparation of a spate of derivatives of the parent 2π -electron three-membered system has been accomplished.² The existence of the cyclopropenyl cation in these derivatives has been established by chemical and spectral methods. The three-membered framework with the 2π electrons is of considerable theoretical interest. Heretofore, in molecular orbital calculations, TPP⁺ has been tacitly assumed planar.³ A knowledge of the

(1) R. Breslow, *J. Am. Chem. Soc.*, **79**, 5318 (1957); R. Breslow and C. Yuan, *ibid.*, **80**, 5991 (1958).

(2) R. Breslow, J. Lockhart, and H. W. Chang, *ibid.*, **83**, 2375 (1961); R. Breslow, H. Höver, and H. W. Chang, *ibid.*, **84**, 3168 (1962).

(3) D. A. Bochvar, I. V. Stankevich, and A. L. Chistiakov, *Russ. J. Phys. Chem.*, **33**, 593 (1959); *Bull. Acad. Sci. USSR (English Transl.)*,