

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.

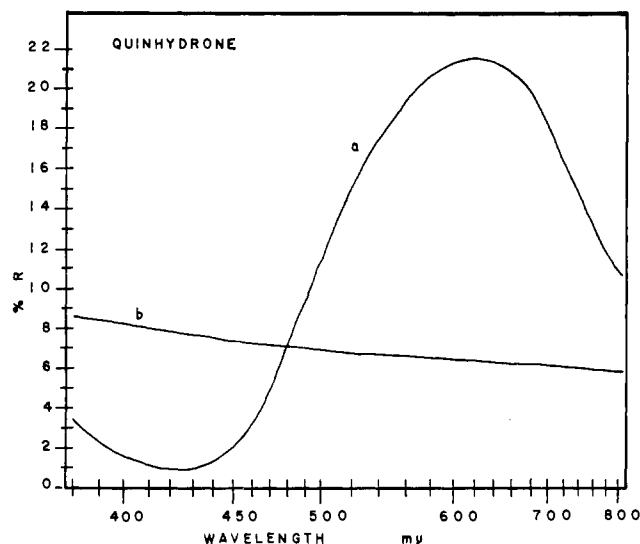


Fig. 2.—Reflection spectra obtained on the (001) face of quinhydrone. a: Light polarized with its electric vector parallel to a ; b: Light polarized with its electric vector parallel to b . The abscissa is linear in energy.

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.

STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT

BASIL G. ANEX
LAWRENCE J. PARKHURST¹¹

RECEIVED AUGUST 16, 1963

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.),

geometry of the cation is important for the computation of delocalization energy, charge density distribution, and bond orders. With this in mind, a crystallographic investigation of *sym*-triphenylcyclopropenyl perchlorate (TPP⁺ClO₄⁻) was undertaken. A microcrystalline sample of this salt was kindly supplied by Professor Ronald Breslow of Columbia University.

Experimental.—Single crystals of *sym*-triphenylcyclopropenyl perchlorate (C₂₁H₁₅ClO₄) adequate for the present investigation were crystallized from acetonitrile. The crystals are monoclinic, elongated along *b*. The following unit-cell parameters were determined from oscillation and Weissenberg photographs using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$): $a = 9.97 \text{ \AA}$, $b = 12.05 \text{ \AA}$, $c = 17.28 \text{ \AA}$, and $\beta = 120^\circ$. The space group is P2₁/c. Equi-inclination Weissenberg photographs of the ten levels, $h0l$ – $h9l$, were collected employing the multiple film technique. Intensities were eye-estimated by comparison with a calibrated intensity strip and the usual Lorentz and polarization corrections applied. Photometered unidimensionally integrated Weissenberg $0kl$ and $2kl$ data were used to correlate the separate layers.

Structure Determination.—The molecular orientation in the crystal was clearly indicated by the spectra $\bar{3}014$ and 602 . The occurrence of high vector density at $\frac{1}{2}, 0$; $0, \frac{1}{2}$; and $\frac{1}{2}, \frac{1}{2}$ in addition to the origin peak in the ($h0l$) Patterson projection limited the possible positions of the molecule in the unit-cell. In the Harker section of the 3-dimensional Patterson function there are four outstandingly high peaks. These are evidently Cl–Cl interactions, one pair being Harker peaks and the other non-Harker. This feature indicates that the Cl atoms are located in or near the glide planes. Preliminary structure factor calculations and packing considerations were used as a validity check.

Approximate O atom coordinates were taken from a partial F_o synthesis in the region of ClO₄⁻ calculated with phases based on the Cl position. Further structure factor–Fourier computations with the Cl and 4 O atoms showed many peaks distributed in hexagonal and fragmented hexagonal pattern throughout the unit cell. In this conglomeration of peaks it was possible to identify quite distinctly the cyclopropenyl ring and the phenyl group attached to C-1. Inclusion of these 9 carbon atoms in the next round of structure factor and Fourier calculation yielded no new information. At this stage it was decided to compute a set of structure factors assuming an essentially planar TPP cation fitted as indicated by the 3-dimensional Patterson function. The observed slight decrease in the R factor was disturbing. Since the shifts in O atom coordinates had been small, it was suspected that their positions might be in error. Accordingly, the oxygen atoms were omitted in the following structure factor calculation. The R factor decreased dramatically and the F_o synthesis indicated the correct oxygen positions. Subsequent refinement was by full matrix least squares and the structure converged rapidly to the present R value of 13%. Further refinement of the structure is in progress.

Discussion.—The structure is composed of TPP cations and ClO₄ anions. The center of the cyclopropenyl group is coincident with the 2₁ axes, sandwiched between the anions, while the anions (nuts) are tightly held by pairs of cations (nutcrackers). The cyclopropenyl ring and the three phenyl atoms attached to it lie approximately in a plane. The average C–C distance in the cyclopropenyl ring is 1.40 \AA , and the

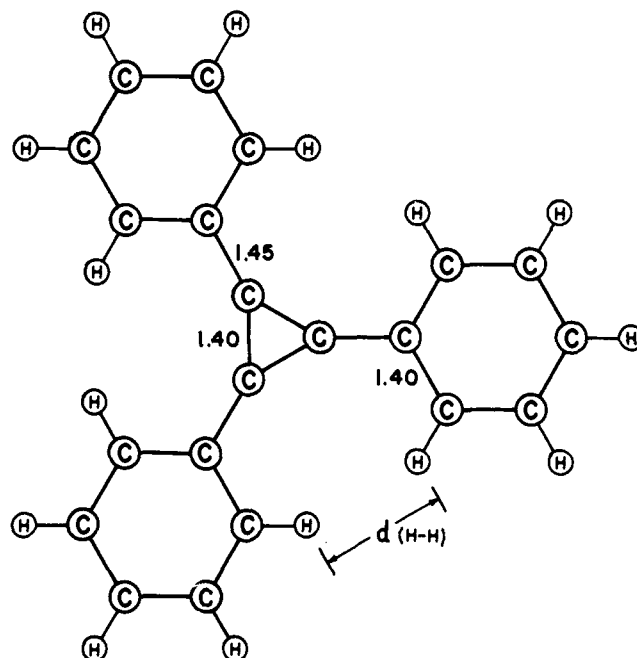


Fig. 1.— $d_{\text{H-H}} = 2.18 \text{ \AA}$ for a C–H distance of 1.0 \AA , and C–C distances as shown, assuming a planar configuration.

average exocyclic C–C “single” bond length is 1.45 \AA . The *sym*-triphenylcyclopropenyl cation has been assumed planar.³ While this would result in rather severe compression of H atoms, the uncertainty in the C–C bond lengths was felt to be sufficient to relieve it. Contrary to these earlier assumptions, the *sym*-triphenylcyclopropenyl cation as a whole is nonplanar; the phenyl groups are twisted out of the plane of the cyclopropenyl group at an average angle of 21°. From these dimensions and an assumed C–H length of 1 \AA , the calculated “ortho” H–H distance for a planar TPP cation is 2.18 \AA , about 0.2 \AA shorter than the sum of the van der Waals radius for hydrogen. The observed nonplanarity is just sufficient to accommodate these atoms with a normal radius.

Acknowledgment.—M. S. is indebted to Professor G. A. Jeffrey, University of Pittsburgh, for his encouragement and the award of a Research Associateship during the tenure of which the experimental work was performed. He is grateful to Professor Ronald Breslow, Columbia University, for a lavish supply of the sample. We wish to thank the National Institutes of Health and the U. S. Public Health Service for Grants GM-10828 E1423, respectively.

DEPARTMENT OF BIOLOGICAL STRUCTURE M. SUNDARALINGAM
UNIVERSITY OF WASHINGTON L. H. JENSEN
SEATTLE, WASHINGTON
CRYSTALLOGRAPHY LABORATORY
UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA

RECEIVED JUNE 17, 1963

Reactions of Amines. XII. The Structure of α -Lactams^{1,2}

Sir:

The intermediate isolated in the Favorskii-like rearrangement of *N*-*t*-butyl-*N*-chlorophenylacetamide **1** has been assigned tentatively the α -lactam structure, 1-*t*-butyl-3-phenylaziridinone (**3**).³

(1) Paper XI: *J. Org. Chem.*, **28**, 2369 (1963).

(2) This work was supported in part by Grant G-21405 from the National Science Foundation and by grants from the John Simon Guggenheim Memorial Foundation and the University of Nebraska Research Council to H. E. B.