Comparison of c.d. curves with corresponding ultraviolet absorption spectra (Fig. 2 and 3) shows that c.d. maxima are located at slightly longer wave lengths than the corresponding ultraviolet absorption maxima, Table I. This comparison of c.d. and absorption spectra permits the uncovering of hidden or overlapping weak absorption bands not detectable by standard ultraviolet spectral technique. Also, it can be observed that the absorption spectrum of poly A contains a shoulder near 270 mμ in agreement with a previous observation.[1]

Additional information about the nature of electronic transitions related to polymer conformation are provided by the apparent partial dissymmetry factor g'[9] (Fig. 2, 3) of poly A and poly C. It appears that the maximum values of the dissymmetry factor g' are located on the long wave-length side of the strong ultraviolet absorption band. Thus, the regions of weak absorption for poly A and poly C, 265–285 and 277–295 mμ, respectively, are strongly optically active. In agreement with previous studies on the nature of electronic transitions in purines and pyrimidines[10] and with dichroic absorption studies on oriented polynucleotide, films[11] and nucleic acids,[2] the present study suggests that the "allowedness" of the n $\rightarrow$ π^* transition is related to the helical structure of these polynucleotides.[12] Further support for this suggestion is provided by the apparent value of the g' factor indicated in Fig. 2 and 3; these values probably represent an *underestimate*[13] at least by a factor of ten. More realistic values of the g' factor would be about 0.05 for poly A and 0.04 for poly C, indicative of a magnetic dipole transition.[14]

The present c.d. data are qualitatively consistent with the previous optical rotatory dispersion results on nucleic acids,[2] which contain complex, not readily resolved dispersion curves in the ultraviolet region. These observations of the circular dichroism of homopolynucleotides indicate that it is a sensitive method for defining the optical rotatory contribution of individual optically active transitions and can be used as a useful tool for the studies of macromolecular conformation.[15,16]

(9) Partial dissymmetry factor introduced by Kuhn g' is given by the ratio ($\epsilon_L - \epsilon_R$)/ϵ at a given wave length. W. Kuhn, *Trans. Faraday Soc.*, **46**, 293 (1930); S. F. Mason, *Mol. Phys.*, **5**, 343 (1962).

(10) S. F. Mason in Special Publications, No. 3, The Chemical Society, (London), 1955, p. 139.

(11) A. Rich and M. Kasha, *J. Am. Chem. Soc.*, **82**, 6196 (1960).

(12) This explanation cannot exclude definitely the attribution of these dichroic absorption bands to a $\pi \rightarrow \pi^*$ transition (see Gellert M., *ibid.*, **83**, 4661, 1961, and ref. 2).

(13) The n $\rightarrow$ π^* absorption bands are of intrinsically low intensity being at most one-tenth as intense as the $\pi \rightarrow \pi^*$ bands (M. Kasha in "Light and Life," Johns Hopkins University Press, Baltimore, Md., 1960).

(14) S. F. Mason, *Quart. Rev.* (London), **17**, 20 (1963).

(15) J. Brahms and G. Spach, *Nature*, in press.

(16) G. Holzworth, W. B. Gratzer, and P. Doty, *J. Am. Chem. Soc.*, **84**, 3194 (1962).

(17) The author is indebted to Professor Ch. Sadron, in whose laboratory this work was done, and M. Daune for valuable advice and stimulating discussions. The author is very grateful to Prof. G. Ourisson, Mr. P. Witz, and Miss H. Hermann, whose generosity and guidance made possible the circular dichroism measurements. Financial support from the Canadian Muscular Dystrophy Association is gratefully acknowledged.

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## Intramolecular Reactions in Acylation of the Cyclooctatetraene Dianion

Sir:

One of the important developments of modern structural theory has been the demonstration of the existence[1a,b] and aromatic character[1b] of the cyclo-

(1) (a) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann.*, **560**, 1 (1948); (b) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784, 3785 (1960).

octatetraene dianion (I). The utility and chemistry of I have not been described other than its acylation[2a–c] and alkylation[2b] to give unspecified isomers of diacyl- and dialkylcyclooctatrienes, its carboxylation to 2,5,7-cyclooctatriene-1,4-dicarboxylic acid,[1a] and its condensation with aldehydes and ketones[2b,d] to yield 7,8-bis(α-hydroxyalkyl)cyclooctatrienes.[2e] The acylation of I has been presently reinvestigated and acylcyclooctatrienes were not obtained; a series of novel condensation products was formed, however, which illustrate the varied chemistry of I and its potential as an intermediate in synthesis.

Addition of an ether solution of I[1b] to excess acetyl chloride (eq. 1) at 0° and isolation of products gave 9-acetoxy-9-methylbicyclo[4.2.1]nonatriene (II, 13%), 9-methylbicyclo[4.2.1]nonatrien-9-ol (III, 19%), 1,8-diacetyl-1,3,5,7-octatetraene (V, 1%), 9-acetoxy-9-methylbicyclo[6.1.0]nonatriene (VI, 22%), polymer, and amorphous hygroscopic material (15%).[3]

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-(CH=CH)_4-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

V
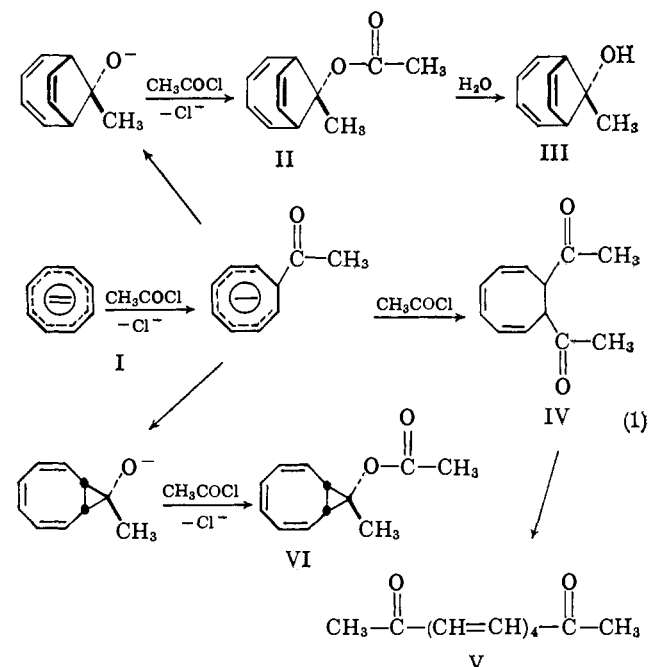
Hydrogenation of II,[3–5] m.p. 48–48.5°, over palladium–charcoal followed by reduction with lithium aluminum hydride (eq. 2) gave 9-methylbicyclo[4.2.1]nonan-9-ol[3] (VII, m.p. 54–55°). Catalytic hydrogenation of III,[3,6] b.p. 36–37° (0.6 mm.), also yielded VII; II is, thus, the acetate of III. The structure of VII[3] was established by its identity with 9-methylbicyclo[4.2.1]nonan-9-ol (VII) prepared from bicyclo[4.2.1]nonan-9-one[7] (VIII) and methylmagnesium iodide (eq. 2). The stereochemistry at C-9 in VII (and thus in II and III) is assigned as indicated since molecular models reveal that attack of the Grignard reagent from the side of

(2) (a) V. D. Azatyan, *Dokl. Akad. Nauk SSSR*, **98**, 403 (1954); (b) V. D. Azatyan and R. S. Gyuli-Kevkhyan, *Dokl. Akad. Nauk Armyan SSR*, **20**, 81 (1955); (c) V. D. Azatyan, R. S. Gyuli-Kevkhyan, L. K. Freidlin, and B. D. Polkovnikov, *Izvest. Akad. Nauk SSR, Ser. Khim. Nauk*, **10**, No. 1, 55 (1957); (d) G. Wittig and D. Wittenberg, *Ann.*, **606**, 1 (1957); (e) Note Added in Proof.—For the recent conversion of I to the cyclononatetraenyl anion see T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **85**, 2852 (1963), and E. A. LaLancette and R. E. Benson, *ibid.*, **85**, 2853 (1963).

(3) (a) All new compounds indicated gave proper analyses. (b) The n.m.r. spectra of the compounds reported herein will be described completely in subsequent papers.
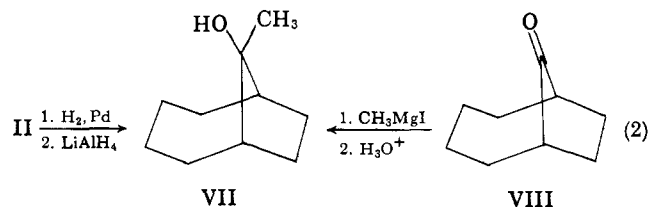
(4) Acidification of this intermediate will also yield III.

(5) Ultraviolet absorption: λ_{max}^{MeOH} 265 (3600), 256 (3750), and 219 mμ (3200); infrared absorption: 5.76, 8.06, and 8.19 μ (ester group).

(6) Ultraviolet absorption: λ_{max}^{MeOH} 260 mμ (ϵ 6300); infrared absorption: 2.80 μ (hydroxyl).

(7) (a) C. D. Gutsche and T. D. Smith, *J. Am. Chem. Soc.*, **82**, 4067 (1960); (b) we are grateful to Dr. Gutsche for the gift of VIII.

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

$$\text{II} \xrightarrow[\text{2. LiAlH}_4]{\text{1. H}_2, \text{Pd}} \text{VII} \xleftarrow[\text{2. H}_3\text{O}^+]{\text{1. CH}_3\text{MgI}} \text{VIII} \quad (2)$$

The acyclic tetraene (V) is an air-sensitive yellow solid, m.p. 106–107°.[8] 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-acetyl-cyclooctene with lead tetraacetate to give the 3-acetoxy-Δ^1-pyrazoline which on pyrolysis yielded a mixture from which X[11] 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 XII[13] 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]nonane[3] (XIV, m.p. 119–120°) which was converted by lithium aluminum hydride to 9-phenylbicyclo[4.2.1]nonan-9-ol[3] (XV, 59–59.5°), identical with that prepared from VIII and phenylmagnesium bromide. The identity of XIII[3] (yellow needles, m.p. 172–173°, λ_{max} 378 mμ (ϵ 47,000))[14] was confirmed by its hydrogenation to

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 Quinhydrone[1]

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

(8) Ultraviolet absorption: λ_{max}^{MeOH} 343 (49,500) and 221 mμ (ϵ 4100); infrared absorption: 5.94 mμ (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: λ_{max}^{MeOH} 247 mμ (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 ~260–265 mμ) 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: λ_{max}^{MeOH} 266 (2900), 258 (3050), and 224 mμ (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 mμ (ϵ 69,000). 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) 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.