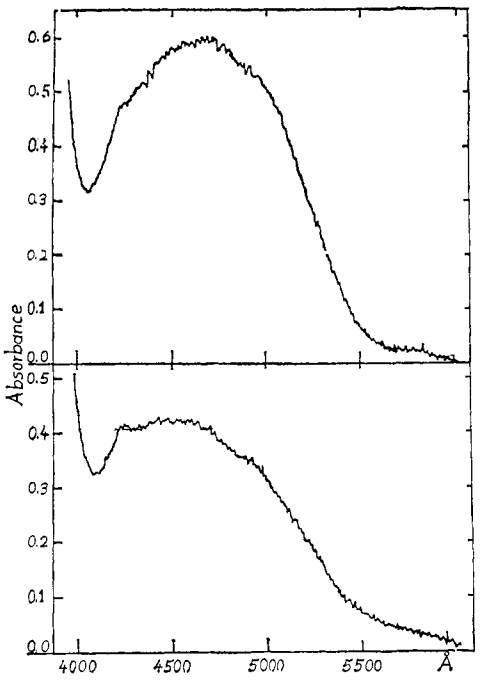

Figure 2. Spectra of a 10^{-4} M solution of $(CH_3)_2NC_6H_4N{=}NC_6H_4NO_2$ in a 1.9:1 by weight mixture of cholesteryl chloride and cholesteryl myristate (T_{nem} = 40°). The sample was aligned for 12 hr at 35° and 20 kOe. In the upper spectrum the electric vector of the light is perpendicular, and in the lower spectrum parallel, to the magnetic field.

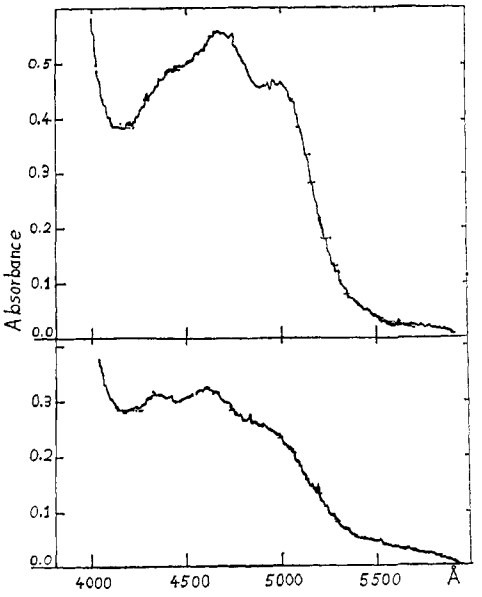

Figure 3. Spectra of 5×10^{-4} M β-carotene in the same solvent as Figure 2. The sample was aligned for 12 hr at 35° and 20 kOe. In the upper spectrum the electric vector of the light is perpendicular, and in the lower spectrum parallel, to the magnetic field.

From this it follows that the transition corresponding to the visible band is polarized in the direction of the long molecular axis.

In Figure 4 the spectra of octa-*t*-butyldiphenoquinone are given. In this case the absorption coefficient for light polarized parallel to the magnetic field is larger by a factor of 1.5. It is again reasonable to assume that the dye molecule is aligned with its long molecular axis perpendicular to the magnetic field. The 4250-Å

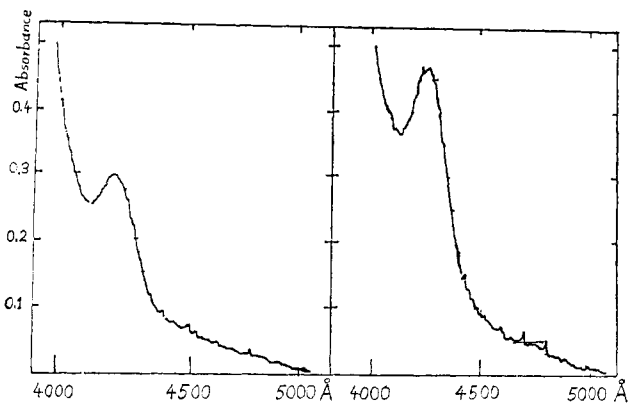

Figure 4. Spectra of octa-*t*-butyldibenzoquinone in the same solvent as Figure 1. The sample was aligned for 12 hr at 20 kOe and 35°. In the right-hand spectrum the electric vector of the light is parallel, and in the left-hand spectrum perpendicular, to the magnetic field.

transition is therefore polarized in the short molecular axis. This is in accordance with theoretical work on the electronic structure of diphenoquinone.[3] In the same way it has been confirmed that in benzoquinone the absorption in the visible is predominantly polarized along the long molecular axis.[4] For 2,3-benzanthracene a short axis polarization of the long-wavelength transition follows in accordance with the theoretical work of Pariser.[5]

From these examples it follows that absorption experiments of oriented molecules in an ordered liquid crystal matrix give valuable information about the polarization of optical transitions. For small molecules which are not as well aligned as those investigated here, the differences in the polarized absorption spectra may be too small to be observable. It seems probable that other liquid crystal solvents can be found in which the dye molecules align better and which form glasses with less light scattering.

Acknowledgment. The author gratefully acknowledges encouraging discussions and help of S. Meiboom, P. M. Rentzepis, L. C. Snyder, R. E. Dietz, and A. E. Meixner.

(3) A. Kuboyama, *Bull. Chem. Soc. Japan*, 33, 917 (1960).
(4) J. M. Hollas, *Spectrochim. Acta*, 20, 1563 (1964).
(5) R. Pariser, *J. Chem. Phys.*, 24, 250 (1956).
(6) On leave of absence from the Max-Planck Institut für Spektroskopie, Göttingen, Germany.

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Benzocarborane

Sir:

Benzocarborane has two different types of delocalized bonding systems fused together, the benzene ring sharing an edge with the icosahedral carborane nucleus (Figure 1). Although the very stable carborane system obviously has highly delocalized bonding electrons,[1] previous investigations have not indicated that the

(1) Review: R. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, Inc., New York, N. Y., 1968, pp 32–54.

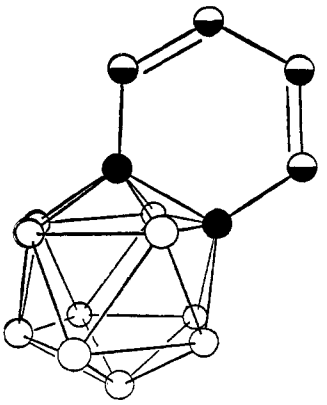


Figure 1. The proposed structure of benzocarborane (1,2-benzo-1,2-dicarba-*closo*-dodecaborane). Open circles are BH, filled circles C, half-filled CH.

ring. 1,2-Dilithiocarborane[5] from 2.9 g of *o*-carborane and 45 mmol of butyllithium in 40 ml of ether was refluxed 5 hr with 2.7 g of *cis*-1,4-dichloro-2-butene.[6] Treatment of the mixture with water followed by chromatography of the ether-soluble product on alumina with cyclohexane as the eluting solvent yielded 1.5 g (38%) of 1,4-dihydrobenzocarborane (**1**), further purified by sublimation and recrystallization from methylcyclohexane, mp 113–114°, nmr (CCl_4) τ 4.35 (t, J = 1.5 Hz, 2H) and τ 7.0 (broadened single peak, 4H), mass spectrum *m/e* up to 198, base peak 195 instead of 196 due to H loss.[7]

Dehydrogenation of **1** was accomplished by refluxing with an equimolar amount of N-bromosuccinimide and a catalytic amount of azobisisobutyronitrile in carbon tetrachloride for 6 hr. Benzocarborane (**2**) was obtained in 30% yield after chromatography on alumina,

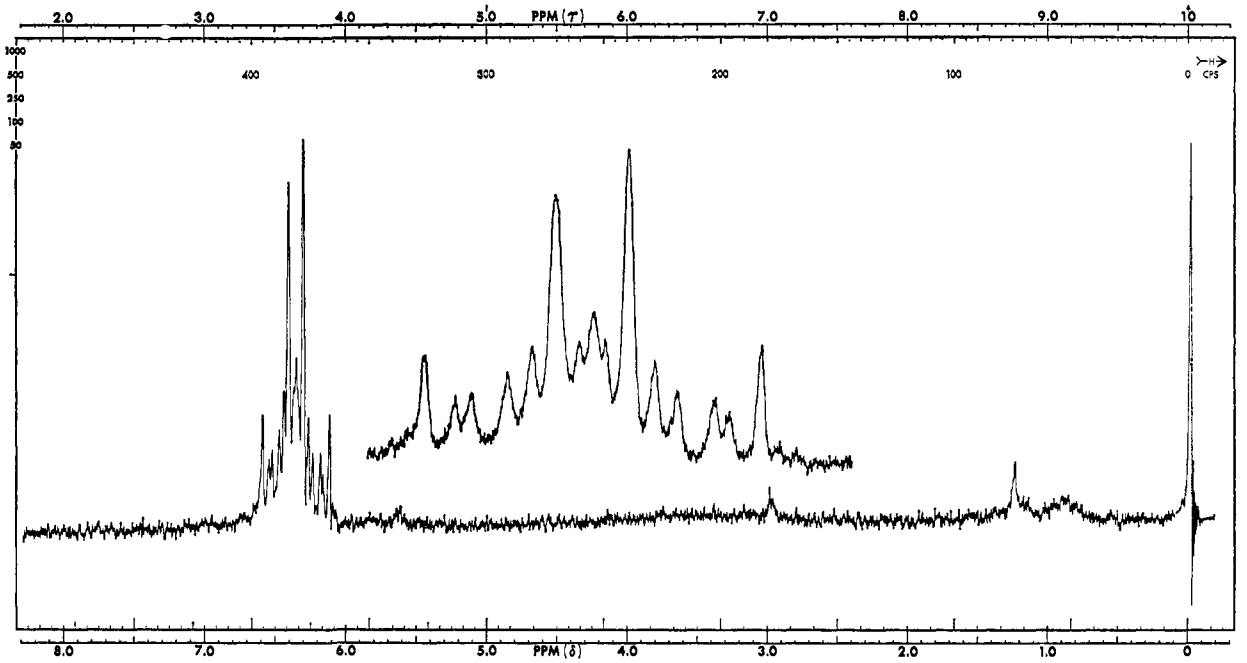
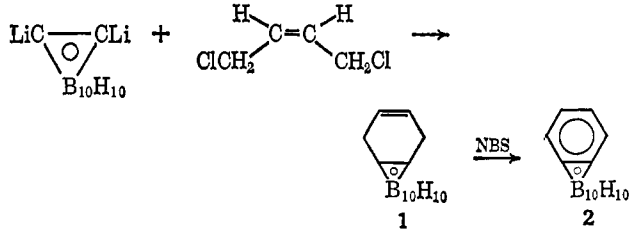


Figure 2. The nmr spectrum of benzocarborane in CCl_4, sweep widths 500 and 100 Hz. Impurities appear at τ 4.35 and 7.0 (dihydrobenzocarborane) and 8.7 (unknown, perhaps tetramethylsuccinonitrile from the initiator).

"aromatic" carborane nucleus can conjugate appreciably with organic π-bond systems.[2,3] Evidence has been presented for apical–apical conjugation through the $B_{10}H_{10}^{2-}$ system.[4]

We have synthesized benzocarborane by a straightforward route and have found that its spectral properties indicate partial aromatic character in the benzenoid



recrystallization from methanol–water, and sublimation, mp 110–110°. Separation from unreacted **1** is difficult. The nmr spectrum of benzocarborane consists of an A_2B_2 multiplet centered at τ 3.63 (Figure 2), which is in between the values usually observed for benzenoid compounds and those of olefins. The ultraviolet spectrum (Figure 3) has the characteristic pattern of benzenoid compounds, though the peak at 260.5 nm, ϵ_{max} 2860, is ~12 times more intense than the corresponding band of benzene; mass spectrum, *m/e* 194.[7]

Benzocarborane is unaffected by (and only slightly soluble in) concentrated sulfuric acid at 100°. It does not react with bromine in carbon tetrachloride, but is attacked (somewhat sluggishly) by potassium permanganate in acetone.

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(7) Satisfactory microanalyses were obtained for C, H, and B.

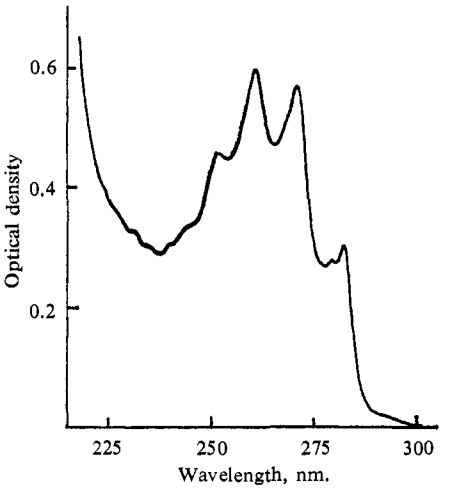
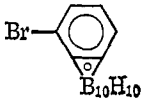


Figure 3. The ultraviolet spectrum of benzocarborane, 2.17×10^{-4} *M* in 2,2,4-trimethylpentane (recorded on a Cary Model 14).

When an excess of N-bromosuccinimide was used for the dehydrogenation of dihydrobenzocarborane (**1**), a less volatile by-product believed to be 1-bromobenzocarborane (**3**) was also obtained, mp 90–92°, nmr (CCl_4) τ 3.22 (t, J = 1.5 Hz, 1H) and τ 3.58 (m, 2H), *m/e* 273.



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(8) (a) Alfred P. Sloan Foundation Fellow; (b) supported by Research Grant No. CA-05513 from the National Cancer Institute, U. S. Public Health Service.

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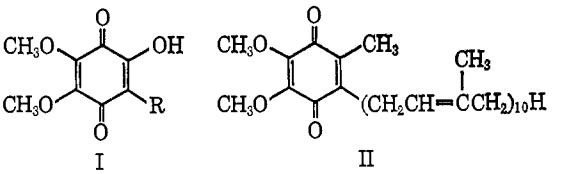
New Hydroxyquinones, Apparent Inhibitors of Coenzyme Q Enzyme Systems[1]

Sir:

New 2,3-dimethoxy-5-hydroxy-6-alkyl-1,4-benzoquinones (I)[2] have been synthesized by procedures that permit considerable structural variations. The alkyl groups are aliphatic, including isoprenoid. These 5-hydroxy analogs of coenzyme Q_{10} (II) are of particular interest for both *in vitro* and *in vivo* studies on the mechanism of the vitamin-like activity of coenzyme Q. The significant structural difference between these analogs and coenzyme Q is the presence of the 5-hydroxy group, instead of the 5-methyl group, which alters the redox characteristics of the quinone. Initial studies, *in vitro*, show that some of these 5-hydroxy analogs strongly inhibit succinoxidase and DPNH oxidase in an intact mitochondrial system or one which is extracted for removal of coenzyme Q_{10}.

The 5-hydroxy analogs were synthesized by complementary alkylation procedures. Where the 6-alkyl group is isoprenoid, the quinones were prepared by the



I II

acid-catalyzed alkylation[3] of 1,4,5-trihydroxy-2,3-dimethoxybenzene[4] with the appropriate allyl alcohol. The isoprenoid hydroquinones obtained were air oxidized during purification. Geranyl, farnesyl, tetraprenyl, solanesyl, decaprenyl, and phytyl derivatives were prepared in this manner. Catalytic reduction of the phytyl derivative (10% Pd–C, EtOH) gave the corresponding dihydrophytyl derivative.

Where the 6-alkyl group is nonisoprenoid, these compounds were prepared by the thermal decomposition of the appropriate diacyl peroxide[5] in the presence of 2,3-dimethoxy-5-hydroxy-1,4-benzoquinone. By this reaction, the pentadecyl, heptadecyl, nonadecyl, and 8′,11′,14′-heptadecatrienyl derivatives were prepared.

Difficulty was originally encountered in synthesizing the 2,3-dimethoxy-5-hydroxy-6-alkyl-1,4-benzoquinones due to low yields in preparing 2,3-dimethoxy-1,4-benzoquinone. It was found that this precursor of 1,4,5-trihydroxy-2,3-dimethoxybenzene can be prepared in good yield from 2,3-dimethoxyphenol by an improvement of the procedure of Smith, *et al.*[6] Also, the alkylation procedures gave very complex mixtures, and the desired products have only limited stability to the normal, tlc, purification procedures. It was found that these 5-hydroxy analogs have certain color characteristics which provided guidance for their isolation. On a silica gel G plate the quinone is violet, while it is yellow in organic solvents and red in solid form. Although reasonable stability was found upon thin-layer chromatography on silica gel G plates developed with 4:1 benzene–methanol, the hydroxyquinones do partially change to a second violet substance, with the same R_f, which is violet in organic solvents. Ultimately, it was observed that the hydroxyquinone can be selectively eluted from the silica gel with ether; the decomposition product is eluted with methanol. The hydroxyquinone can also be purified by chromatography on a silica gel column by eluting with hexane containing increasing increments of ether.

The structures of these new hydroxy analogs of coenzyme Q are appropriately assigned by their spectra (Table I).

Initial studies have been made on the activity, *in vitro*, of these new hydroxy analogs of coenzyme Q in mitochondrial succinoxidase and DPNH-oxidase systems which are either intact or extracted for removal of coenzyme Q_{10}.[7] These studies reveal that some of the compounds do have significant inhibitory activity.

The data in Table II show the *in vitro* activity in the succinoxidase system for enzyme preparations which have not been extracted for removal of coenzyme Q_{10}. The farnesyl, solanesyl, phytyl, dihydrophytyl, and

(1) Coenzyme Q. CIII.
(2) For R, see Table I.
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