ciently and *with complete retention of chirality*[8a,b] by the sequence **1–4** (Scheme I).

Attempts at the direct displacement of (−)-π-bromocamphor (**4**) or its 1,3-dioxolane derivative with dimethyl malonate anion failed. Therefore, we prepared (−)-π-iodocamphor (**5**) using a threefold excess of anhydrous potassium iodide[10] in freshly distilled dimethylformamide (DMF) at 110 °C in nearly quantitative yield (Scheme II). In contrast to the bromo derivative, reaction of the latter intermediate with 10 equiv of the sodium salt of dimethyl malonate in refluxing DMF (17 h) provided (−)-keto ester **6**[11,12] (60%). The displacement was accompanied by concommitant decarbomethoxylation (presumably via attack of displaced iodide on the initially formed diester[13]). Oximation of **6** was carried out by standard means and the resultant (+)-oximino ester (**7**)[14] exposed to *p*-toluenesulfonyl chloride in pyridine to induce Beckmann fragmentation[16] (70%). The resultant mixture of double bond isomers (**8** and **9**) readily converged to the more stable endocyclic (−)-cyano ester **9** when treated with anhydrous trifluoroacetic acid. Cyclization of **9** to (+)-cyano ketone **10** proceeded unidirectionally in 70% yield[11] using potassium *tert*-butoxide in tetrahydrofuran. The use of similar C,D intermediates in the total synthesis of steroids has been dealt with elsewhere.[4c,d] For example, in a preliminary study on the subsequent deployment of **10**, we have found that it reacts readily with methyl vinyl ketone[17] to afford a mixture of tricyclenone **11** and hydroxy ketone **12** and that the latter substance can be dehydrated to **11** when exposed to $POCl_3$-pyridine. Further studies to utilize these intermediates in the total synthesis of several steroids is under active investigation.

Acknowledgment. The generous support of the National Science Foundation (CHE75-09869) is gratefully acknowledged.

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(10) We found potassium iodide to be the reagent of choice for this reaction since the potassium bromide formed precipitates out of the hot DMF solution.

(11) We have made no attempts to optimize the yields in this sequence.

(12) All new compounds exhibited satisfactory chiroptic and spectroscopic properties (IR, NMR, mass spectroscopy). The key intermediates **6–11** showed satisfactory exact mass composition of their molecular ions.

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An Experimental Determination of "Bonding Charge" in Carbon-Carbon Bonds

Sir:

Many attempts have been made to understand the nature of the chemical bond by correlating bond length with theoretically derived quantities such as bond order, electronegativity, hybridization, and ionic character.[1] In this communication we provide estimates of the amount of charge in various C-C bonds and a correlation between bonding charge and bond length, both quantitites being experimentally derived.

In recent years accurate x-ray (and neutron) diffraction measurements together with the development of various computational techniques[2] have led to a significant progress in determining the electron density distribution in a chemical bond. Electron density difference maps[3] may be exploited for the calculation of derived quantities as net molecular or ionic charges, dipole and quadrupole moments, atom populations, and "bonding charge" in bonds. Very little has been done in this area, which is still in the stage of definitions and development of methods.[4]

The "net bonding charge"—the amount of charge which migrates to the region between bonded atoms on formation of a molecule—may be defined as the excess charge which accumulates between bonded atoms over the amount that would have occurred in these regions as a consequence of superposition of spherical atoms.

An estimate of the "bonding charge", as defined above, may be obtained from the deformation maps[3] by integrating the positive difference density over the volume of the bond. In cases where the excess density in the bond is completely surrounded by a surface of zero deformation density,[4c] the region of integration is uniquely defined; where the bonding peak is not confined to the region between two bonded atoms, e.g., peaks of adjacent bonds merge,[6b] the number of electrons obtained is affected somewhat by the choice of the integration boundaries.[7]

We have estimated the number of "bonding electrons" in various C-C bonds of several molecules whose electron-density distributions were mapped[4b,c,5,6] using accurate x-ray data measured at low temperatures[4b,c,6,8] and room temperature.[9] The bond lengths varied between 1.26 and 1.57 Å.[10a] The standard deviation in the charge was estimated to be 0.03 e in tetraphenylbutatriene.[10b]

Figure 1, which presents a plot of bonding charge vs. bond length, summarizes the results of this study. Three principal conclusions may be drawn from this plot, which almost falls on a smooth line. (a) The number of "bonding electrons", as defined above, is relatively small; only a fraction of one electron accumulates in the bond; 0.1-0.3 e[11] were found in the range (1.57-1.26 Å) investigated.[12] (b) It is possible to correlate the number of bonding electrons with bond length in C-C bonds belonging to entirely different molecules varying widely in

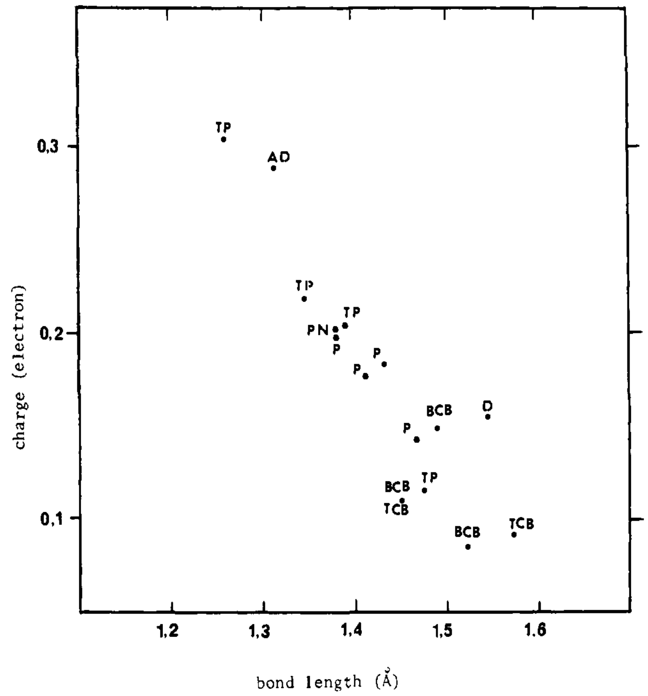

Figure 1. A plot of bonding charge vs. bond length: TP, tetraphenylbutatriene;[4c] AD, allenedicarboxylic acid-acetamide;[6a] PN, *p*-nitropyridine oxide;[6d] D, diamond;[6d] TCB, tetracyanocyclobutane;[4b] P, perylene;[6c] BCB, a bicyclobutane derivative, *exo,exo*-1,3-diethylbicyclobutane-2,4-dicarboxylic acid.[6b]

chemical structure. (c) The number of bonding electrons in various C-C bonds falls off almost linearly with increasing bond length. Assuming the points to lie on a straight line ($y = 0.686x + 1.152$ where y is the charge and x is the bond length) yields a scatter, $(\Sigma\Delta^2/(n-1))^{1/2}$, $n = 16$, of 0.026e which compares favorably with the estimated standard deviation computed for tetraphenylbutatriene.

A similar correlation between the charge in the bond and its length is suggested by a simple electrostatic model of the chemical bond, which supposes that a chemical bond is a result of accumulation of negative charge in the region between bonded atoms to an extent sufficient to balance the nuclear forces of repulsion.[14]

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(12) An extrapolation of the curve to a bond length of 1.20 Å would lead to a bonding charge of 0.4 e for the C≡C triple bond. This excess charge may be correlated with the relatively strong acidic properties of the acetylenic C-H bond.[13]
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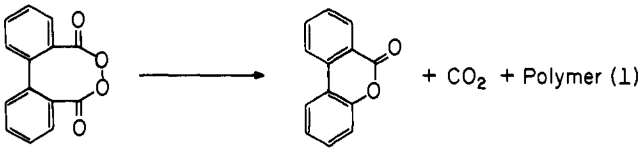
Chemically Initiated Electron Exchange Luminescence. A New Chemiluminescent Reaction Path for Organic Peroxides

Sir:

We would like to report an efficient new chemiluminescent reaction that delineates an apparently important class of chemiluminescent processes and provides insight into several previously reported light-producing reactions. In general, the exothermic decomposition of peroxides to generate directly electronically excited-state carbonyl compounds has formed the basis for nearly all of organic chemiluminescence.[1] In this communication we will outline a reaction sequence in which diphenoyl peroxide (**1**) undergoes chemically initiated electron exchange with an aromatic hydrocarbon to form directly the electronically excited singlet state of the hydrocarbon which, in turn, emits a photon of visible light.

Thermolysis of a dilute solution of diphenoyl peroxide[2] in CH_2Cl_2 at ~24 °C for 24 h resulted in the formation of benzocoumarin (**2**) in 75% yield[3] and polymeric peroxide (eq 1).



1 2

Under these conditions there was virtually no chemiluminescence from this reaction. However, addition of certain aromatic hydrocarbons (see Figure 2) to the reaction mixture resulted in efficient light formation. The spectrum of the emission corresponds in all of the cases studied to the fluorescence of the added hydrocarbon.

Such an observation is not unique among chemiluminescent systems and has been attributed to electronic energy transfer to the added hydrocarbon from a product molecule formed in an excited state. However, in this case, the unusual observation was made that, while 9,10-diphenylanthracene (DPA) was quite effective at promoting light formation, 9,10-dibromoanthracene and biacetyl were essentially completely ineffective.[4] Moreover, incorporation of the aromatic hydrocarbon in the reaction solution increased the rate of consumption of the diphenoyl peroxide. These observations indicate a special interaction of the aromatic hydrocarbon with the peroxide rather than simple energy transfer as the light-forming step.

The chemiluminescence observed from peroxide **1** and aromatic hydrocarbons is strictly first order in peroxide con-