vapor chromatogram. Spectral data for the lumiketones are given in Table III. The mass spectrum for **4e** (mol wt 342) had major peaks at *m/e* 342, 327, 299, 135, 121, 107, 105, 91, 79, 57, 55, 43, and 41 (base peak).

Quantum yields were measured as described previously[8] at 254 ± 10 nm using a Bausch and Lomb Model 33-86-25 high-intensity grating monochromator with a 200-W super-pressure mercury source. The quantitative analysis for the lumiketones was carried out by glpc on an SE-30 column (see below). Measurements were normally made in reagent grade dioxane as solvent. The effect of of possible impurities in the solvent was determined by studying the per cent conversion of **3a** → **4a** with and without added quencher in duplicate solutions in reagent dioxane and dioxane purified by the method of Wiberg.[31] In all cases, yields of **4a** were 10–12% higher in the purified compared with the unpurified dioxane. Accordingly, quantum yield data obtained in unpurified dioxane have been increased by 11% and the corrected data are given in Table IV. Such corrections are not necessary in the quenching experiments (below) where relative product yields with and without added quencher were determined. Data in Table IV are averages of duplicate determinations.

Quenching Studies. All quenching studies were run on a precision "merry-go-round" apparatus immersed in a water bath at 34 ± 1°. A 450-W high-pressure mercury lamp was used as the light source, and Pyrex filters were used to cut out light below 3000 Å. Solutions containing equal amounts of steroid and graduated amounts of quencher were adjusted to 4 ml by the addition of dioxane. The solutions were placed in the merry-go-round and photolyzed for 10–15 min. Tetracosane, as an internal standard, was then added, and the solutions were analyzed for lumiketone by glpc on a 4 ft 10% SE-30 on Chromosorb W, DMCS-A/W column. The 1,3-cyclohexadiene and *trans*-piperylene used as quenchers were obtained from Chemical Samples Co. and distilled before use.

Peaks near the solvent peak on the vapor chromatogram typical of 1,3-cyclohexadiene and *trans*-piperylene dimers were observed in all the runs, and increased in relative size as the extent of quenching increased.

Gas Chromatographic Analysis. The amount of lumiketone was measured by glpc using a $^1/_8$ in. × 4 ft 10% SE-30 on Chromosorb W, DMCS-A/W column. The oven temperature was generally 250–255°, although in certain cases, temperatures from 225 to 260° were used. Measured amounts of tetracosane were added to the lumiketone solutions before analysis.

To determine the gas chromatography response factors, standard solutions of tetracosane and the pure lumiketones were prepared. These factors were redetermined every time an analysis for lumiketone was run, and the standard solution was injected frequently during a run. The retention times for the dienones and lumiketones are listed in Table V along with those of the tetracosane standard.

Table V

Dienone	Oven temp, °C	Retention times,[a] min: Tetracosane	Lumiketone	Dienone
3a	250	2.6	3.6	6.0
3b	225	6.3	7.7	14.7
	240	3.3	4.4	8.0
	255	2.3	3.2	5.6
3c	255	2.3	3.5	6.2
3d	255	2.3	5.1	9.6
3e	255	2.3	4.7	8.2
3f	255	2.3	5.7	11.2

[a] On a $^1/_8$ in. × 4 ft 10% SE-30 on Chromosorb W, DMCS-A/W column. Injection port, 270°.

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Perturbed [12]Annulenes. The Synthesis of Pyracylenes

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Abstract: Utilizing PMO theory, pyracylene is described as a [12]annulene with an internal vinyl cross-link. As such, it should be an unusually good model for a planar [12]annulene. To examine such a hypothesis, the synthesis of pyracylene, 1,2-dibromopyracylene, and 1,2-diphenylpyracylene was achieved. The key step involved a polybenzylic bromination. After introduction of the first bromine, subsequent hydrogen atom removal involved predominantly, if not exclusively, the β-hydrogen trans to that bromine. Iodide-promoted elimination of the thus formed dibromide introduced the crucial bridging double bonds. Polarographic reduction suggested the presence of an empty approximately nonbonding molecular orbital in agreement with the above model. Dramatic support arose from their nmr spectra which show the protons shifted to exceptionally high fields. These abnormal shifts are interpreted in terms of a paramagnetic ring current—in excellent accord with the proposed peripheral electronic model.

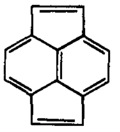
Introduction and Theory

A fundamental question in organic chemistry relates to the net energy change associated with electron delocalization. Inherent in the concepts of resonance theory lies the proposition that electron delocalization increases the stability of the system. Molecular orbital theory refutes that hypothesis and suggests that associated with electron delocalization may be net energy stabilization, no net energy change, or energy destabilization. In the first category fall the well-known $4n + 2$ monocyclic and many related systems; however, experimental verification of the remaining categories remains to be established. Barrelene and [4.4.2]propellapentaene may be representative of molecules in which no net stabilization accompanies electron delocalization.[1] Theory predicts planar $4n$ monocyclic systems belong to the last category for which Dewar and Breslow have coined the term antiaromatics.[2]

Experimental verification is frustrated by the lack of molecular rigidity in most neutral $4n$ monocyclic systems larger than cyclobutadiene. For cyclooctatetraene, a tub conformation has been well established.[3] The structures of the [12]-,[4] [16]-,[5] and [24]annulenes[6] are less secure although the available data clearly indicate nonplanar structures.

To introduce molecular rigidity, we decided to incorporate cross-links into the [$4n$]annulene unit. Clearly, the cross-links must be introduced to minimize the perturbation of the $4n$ monocyclic system. In particular, the chemistry to be associated with such systems mainly derives from a consideration of their frontier orbitals (*i.e.*, the highest occupied and the lowest unoccupied molecular orbitals). In a sense, that system in which these two MO's are near degenerate provides the best model for the planar [$4n$]annulene. Applying Dewar's PMO treatment,[7] we find that simple bond formation between nonadjacent atoms of like parity in a $4n$ monocycle generates a first-order perturbation term of zero for at least one nonbonding orbital, the other becoming slightly bonding or antibonding.[8,9]

A much more intriguing perturbation arises by insertion of an internal π system into a $4n$ monocyclic periphery. The energy change in the molecular orbitals of the interacting π systems may be estimated by Dewar's second-order perturbation expression. Let us consider the particular case of pyracylene (I). The π-electron levels can be approximated by perturbing a 12-electron monocyclic array of D_{2h} symmetry with an internal vinyl moiety as depicted in II. Treatment of the 12 π-electron peripheral basis set by group theory generates a half-filled degenerate pair of nonbonding levels having symmetries as indicated in Chart I. Both ψ_6 and ψ_7 have nonzero coefficients at the perturbation sites. However, mixing of the bonding (S_YS_Z) or antibonding (S_YA_Z) MO's of the vinyl cross-link with ψ_7 (A_YS_Z) of the monocycle is symmetry forbidden and the ψ_7 NB–MO will be unaffected by the vinyl perturbation. The antibonding vinyl MO will interact with ψ_6 of the [12]annulene so as to *lower* the energy of the latter. If the splitting of ψ_6 and ψ_7 may be taken as a measure of the extent of perturbation from the [12]annulene, it is clear from such calculations that the perturbation is indeed small. Using PPP–SCF theory[10] and the Pople first-order configuration interaction method,[11] an estimation of the lowest lying triplet and singlet transition energies (Δ^3E and Δ^1E, respectively) may be made. The pyracylene Δ^3E and Δ^1E transitions of 2.05 (605 nm) and 2.30 eV (539 nm), respectively, are unusually low lying for such a small molecule.[12]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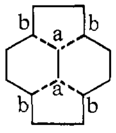
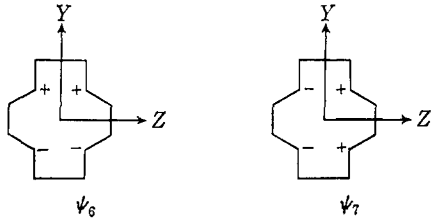


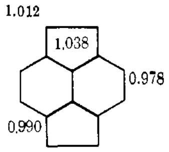
II

Chart I. Symmetry Properties of Nonbonding Levels



The charge distribution in a hydrocarbon also provides insight into the electronic nature of the molecule. From a PPP–SCF calculation, the π-electron densities are as shown in Chart II. Equal (unity) π-electron density at each carbon is a characteristic of alternant conjugated hydrocarbons in Hückel or SCF treatments.[13] Although strictly a nonalternant system, the SCF π-electron density on peripheral positions in neutral pyracylene is nearly unity at each carbon in agreement with the above peripheral electronic model.

Chart II. PPP–SCF π-Electron Densities



One final point to be made regarding pyracylene relates to its strained carbon framework. Bridging both peri positions of naphthalene by short carbon chains inhibits the normal strain releasing mechanism of naphthalenes.[14] Dauben developed an empirical potential function for calculating bending and torsional components of strain energy for hydrocarbons de-

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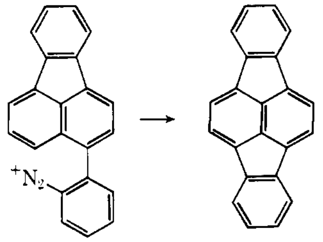
stabilized by angular or torsional deformations.[15] This function is reported to predict strain energies of cycloalkanes and cycloalkenes which are in good agreement with experimental values. From this relationship, pyracylene has been predicted to have a strain energy of 48 kcal/mol.

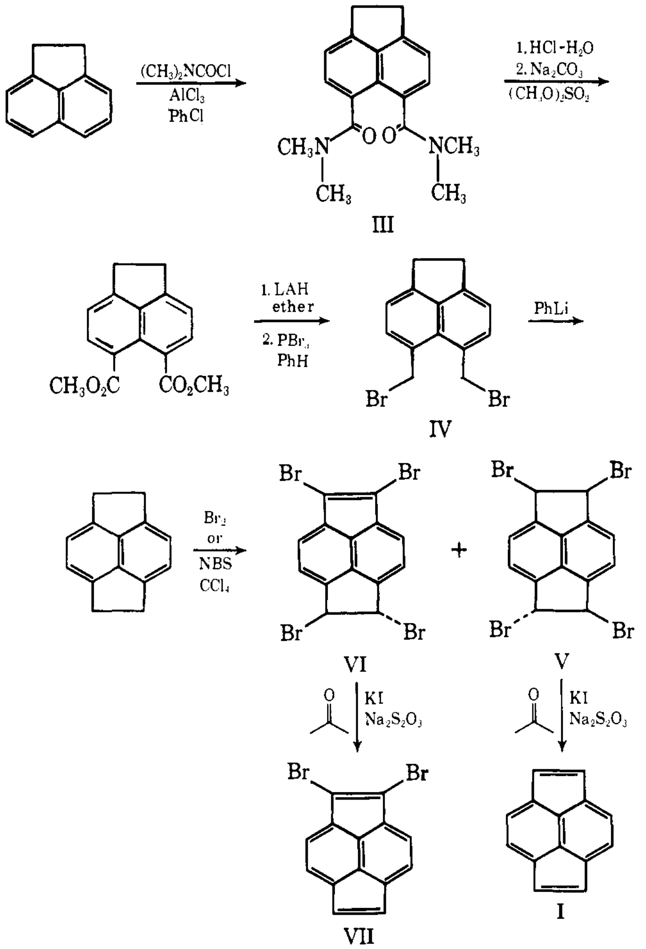
Prior to our work, Stubbs and Tucker[16] reported the cyclization of a diazonium salt to 1,2,5,6-dibenzopyracylene. Anderson and coworkers[17] failed to generate the pyracylene system although they reported the partial dehydrogenation of pyracene to 1,2-dihydropyracylene. Pyracyloquinone, the first simple derivative of the parent system, was reported in 1966.[18] Its properties and those of its simple derivatives provide striking confirmation of the above concepts.[18,19] In this paper, we wish to report the preparation, characterization, and spectroscopic properties of the parent hydrocarbon, pyracylene, and its 1,2-dibromo and 1,2-diphenyl derivatives.[20]



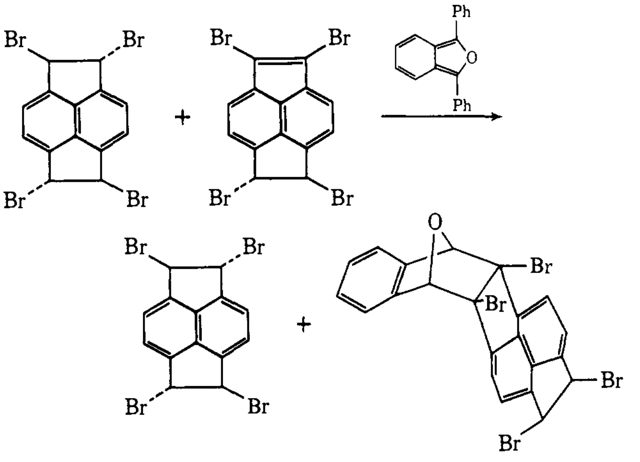
Results and Discussion

Synthesis of Pyracylene and 1,2-Dibromopyracylene. Scheme I outlines the synthesis of both pyracylene and 1,2-dibromopyracylene. The synthesis of pyracene derives from the work of Carpino with modifications (see Experimental Section).[21] The key reaction of the synthesis is the bromination of pyracene. Either the use of *N*-bromosuccinimide or molecular bromine proceeds satisfactorily although the latter is preferable. This reaction produces a mixture of two tetrabromides V and VI in a 3:2 ratio which we refer to as the saturated and unsaturated tetrabromides, respectively. All attempts to control the bromination so as to produce only V failed; even less than stoichiometric quantities of bromine generated a mixture. Chromatographic techniques either failed to separate V and VI or decomposed them. Originally, the separation consisted of a slow recrystallization from ethanol which produced a mixture of colorless crystals (V) and yellow crystals (VI). Separation of the colorless crystals from the yellow ones with a tweezer generated essentially pure V and VI, respectively. Eventually, we devised the chemical separation as shown in Scheme II. The chromatographic properties of the 1:1 Diels–Alder adduct of VI and 1,3-diphenylisobenzofuran[22] are sufficiently different from V to allow their easy separation. The spectral properties of V and VI completely confirmed the assigned structures (see Experimental Section). Reductive elimination of either V or VI with powdered potassium iodide in the presence of sodium thiosulfate in refluxing acetone generated solutions of pyracylene and 1,2-dibromopyracylene, respectively.[23] The spectral properties (*vide infra*) are in complete accord with the assigned structures. Chemical characterization of

Scheme I. Synthesis of Pyracylene and 1,2-Dibromopyracylene



Scheme II. Separation of Saturated and Unsaturated Tetrabromides



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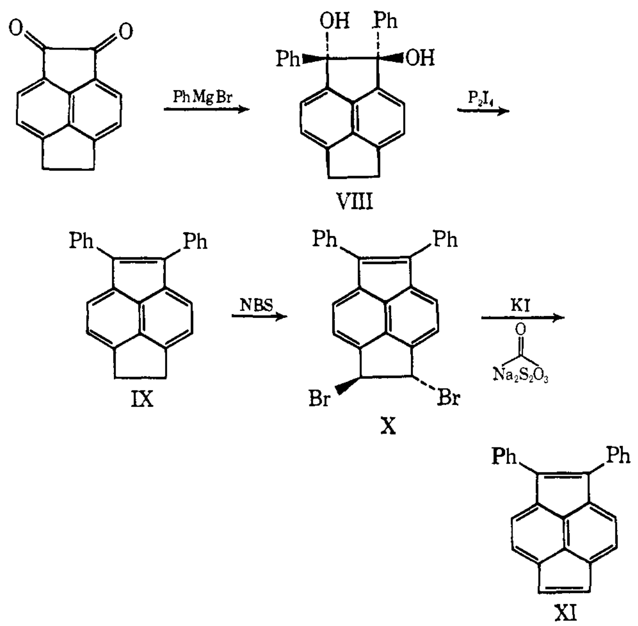
pyracylene was achieved in two ways. Catalytic reduction of I generated pyracene virtually quantitatively (based on starting tetrabromide) and bromine addition in carbon tetrachloride regenerated V. 1,2-Dibromopyracylene was characterized by bromine addition regenerating VI.

Synthesis of 1,2-Diphenylpyracylene. Scheme III outlines the approach to 1,2-diphenylpyracylene.

Scheme III. Synthesis of 1,2-Diphenylpyracylene



Phenylmagnesium bromide addition to 1,2-diketopyracene produces the diol VIII.[24] The absence of any hydrogen-bonded OH absorption in the infrared spectrum allows the assignment of the trans configuration as shown. Reductive cleavage of the hydroxyl groups utilizing diphosphorus tetraiodide[25] generated a quantitative yield of IX.[26] Conversion of IX to XI proceeded as in the previous cases by bromination followed by reductive elimination. Chemical verification for the diphenylpyracylene structure arose through its diimide reduction back to its dihydro derivative IX and through bromine addition to X.

The success of this approach to pyracylenes revolves around the critical bromination step. To examine this reaction more closely, we studied the bromination of IX in some detail. In particular, we were concerned with the effect of a bromine on bromination at a neighboring carbon atom.[27] If 1,2-diphenyl-*cis*-5,6-dideuterio-5,6-dihydropyracylene (XII) is dibrominated, a mixture of three dibromides is produced as illustrated in Scheme IV. The deuterium distributions in the products were analyzed by conversion of the mixture XIV back to a mixture of deuterated dihydropyracylenes and analysis of the latter by mass spectrometry. For this conversion, XIV was treated with iodide ion to cleave the bromides followed by diimide reduction of the unsubstituted double bond. Analysis revealed the deuterium distribution listed in Table I.

Scheme IV. Bromination of a Dihydropyracylene

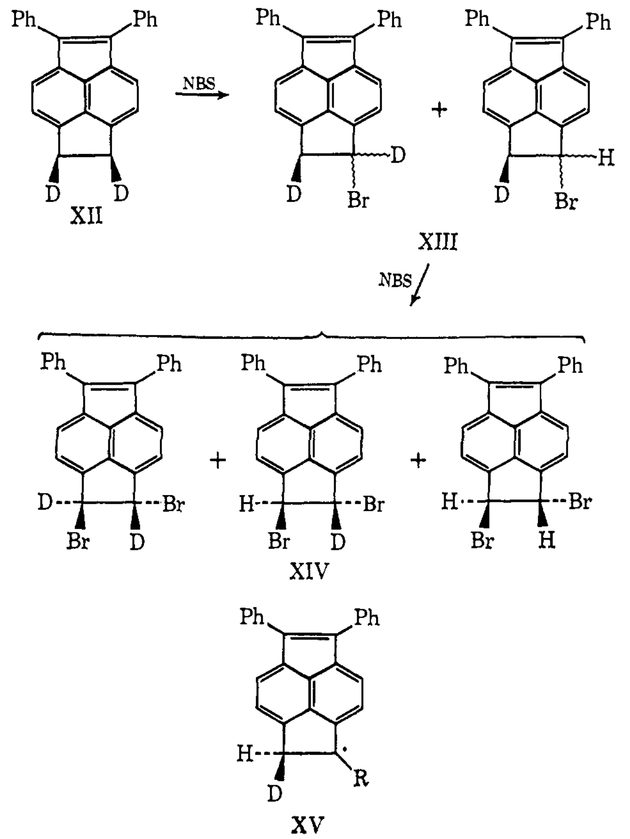


Table I. Deuterium Analysis

	Calcd A^a	Calcd B^b	Exptl
d_2	56.2 ± 0.4	37.5 ± 0.4	37.8
d_1	37.5 ± 0.4	50.0 ± 0.4	48.6
d_0	6.3 ± 0.3	12.5 ± 0.5	13.6

[a] Calculated based on no stereoselectivity in second hydrogen abstraction. [b] Calculated based on trans hydrogen on carbon to bromine being abstracted exclusively.

Two extreme possibilities for abstraction of the second hydrogen must be considered. At one extreme, no stereochemical preference for hydrogen abstraction exists. Thus, the deuterium distribution is merely determined by the deuterium isotope effect for hydrogen abstraction by bromine radical. At the other extreme, removal of hydrogen from the monobromo compound (XII) involves exclusive removal of the trans hydrogen (or deuteron). To calculate the expected distributions for these two cases we assume that capture of the first radical intermediate (XV, R = H or D) is nonstereoselective, *i.e.*, there exists no preference for approach of the incoming bromine atom cis or trans to adjacent deuterium. We next needed the value of the isotope effect for the hydrogen abstraction step. To determine k_H/k_D, we monobrominated XII and analyzed for deuterium content. This analysis indicated a value of 3.0

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± 0.2. Utilizing these data, we calculated the distributions for the two cases listed in Table I.

The data of Table I clearly demonstrate that a strong preference for abstraction of hydrogen trans to neighboring bromine exists. This high stereospecificity combined with the fact that the product possesses bromines exclusively trans to one another indicates a strong influence of neighboring bromine. The high selectivity suggests a more intimate role for bromine than merely its steric bulk directing the incoming radicals trans to itself.

Nmr Spectral Properties. A molecular orbital method for determining the contribution to the magnetic susceptibility in a planar cyclic conjugated hydrocarbon arising from the magnetically induced circulation of its π electrons has been developed by London.[28]

The method has long been used for calculating the (negative) diamagnetic susceptibility associated with π-electron currents in $4n + 2$ systems. More recently, application of the London theory to $4n$ π-electron monocyclic and $4n$ polycyclic systems (the latter formally arising from cross-link perturbations on $4n$ monocyclic peripheries) has shown that magnetically perturbed π electrons in such systems contribute a positive contribution to the magnetic susceptibility, *i.e.*, the induced current is paramagnetic.[29]

Prior to the London treatment, Van Vleck, using perturbation theory, developed a fundamental expression (eq 1) describing the molar magnetic susceptibility component along the principal Z axis $\chi_M(Z)$ of a system of electrons whose ground and excited states are described by eigenfunctions ψ_0 (eigenvalue E_0) and ψ_n (eigenvalue E_n), respectively.[30] In this equation, $\overline{X_i^2 + Y_i^2}$ is a quantum-mechanical expectation value where X_i and Y_i are x–y plane coordinates of electron i,

$$M^{(Z)} = -\frac{Ne^2}{4mc^2}\sum_i \overline{X_i^2 + Y_i^2} + \frac{Ne}{2m^2c^2}\sum_{n\pm 0}\frac{|\langle\psi_0|M_Z|\psi_n\rangle|}{E_n - E_0} \qquad (1)$$

M_Z is the quantum operator for the Z component of angular momentum, and the rest of the symbols have their usual meaning. Longuet-Higgins,[29b] Rebane,[31] and Dorfman[29d] have recently analyzed the induced paramagnetic behavior of $4n$ cyclic π systems with reference to the Van Vleck expression. Thus, induced π-electron paramagnetism or a reduced π-electron diamagnetism is predicted for $4n$ and "perturbed" $4n$ systems. Experimental verification appears to exist in the cases of the [12]-,[4] [16]-,[5] and [24]annulenes.[6]

Table II. Nmr Spectral Properties[a]

Compd	Position 1,2	3	4	5,6
I[b]	6.01	6.52	6.52	6.01
VII[c]		6.60	6.57	6.11
XI[b]		6.61	6.61	6.06
5,6-Dihydro-pyracylene[b]	7.04	7.65	7.32	3.49
IX[b]		7.69	7.35	3.47

[a] All shifts are given in parts per million relative to TMS as an internal standard. [b] Determined as a solution in carbon tetrachloride. [c] Determined as a solution in deuteriochloroform.

Does a paramagnetic ring current exist in pyracylene? The nmr spectral properties for pyracylene and its derivatives are summarized in Table II. For comparison, the spectral properties of the various dihydro compounds are included. It becomes immediately obvious from inspection of the data that both the ethylene bridge protons and the naphthalene ring protons occur at exceptionally high fields compared to the corresponding protons of the dihydro compounds. In completing the peripheral conjugation by going from dihydropyracylene to pyracylene, we see all the vinyl protons shift upfield by over 1 ppm.

Two questions come to mind. Can the shift be associated with any unusual solvation or association effects or can it be due to any unusual negative charge on the periphery? Two experiments rule out the first possibility. First, an examination of the effect of solvent on the chemical shifts of 1,2-dibromopyracylene (see Table III) indicated identical solvent-induced shifts as those of 1,2-dibromoacenaphthylene, a model compound with proton chemical shifts in the normal aromatic region. Thus unusual solvent–solute interactions can be ruled out. That unusual solute–solute interactions are not responsible arises from a dilution study. Decreasing the concentration by over 200-fold to less than 10^{-4} M causes no appreciable change in chemical shifts.

Table III. Solvent-Induced Shifts for 1,2-Dibromopyracylene[a]

Solvent	Position 3	4	5
Acetone	376	402	411
Chloroform-d	367	394	396
Cyclohexane	360	388	388
Benzene-d_6	346	366	371

[a] All shifts are in hertz downfield from internal TMS at 60 Mcps.

An unusually high π-electron charge density in the pyracylene periphery appears equally unlikely as an explanation for the abnormally high-field chemical shifts. The previously mentioned SCF–MO calculations indicate a near-unity π-electron charge density at the pyracylene periphery atoms. In view of the demonstrated general reliability of the SCF–MO method,[2d,10,15] a discrepancy between the SCF calculated pyracylene charge densities and those of the real molecule sufficiently large to account for the shifts is most unlikely.

Support for a paramagnetic ring current as the cause comes from a further consideration of the 1,2-diphenylpyracylene spectrum contrasted with its dihydro and tetrahydro derivatives as depicted in Figure 1. The absorptions for the phenyl rings in the tetrahydro derivative appear at unusually high fields because of their experiencing a mutal shielding effect due to their ring currents. Going to the dihydro compound IX allows them to conjugate, causing them to become effectively

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(28) F. London, *J. Phys. Radium*, **8**, 397 (1937).

(29) (a) J. A. Pople and K. Untch, *J. Amer. Chem. Soc.*, **88**, 4811 (1966); (b) H. C. Longuet-Higgins, "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 109; (v) F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch. A*, **22**, 103 (1967); (d) Y. G. Dorfman, "Diamagnetism and the Chemical Bond," C. P. Poole, Translation Ed., Elsevier, New York, N. Y., 1965, pp 15–16.

(30) (a) J. H. Van Vleck, "Electric and Magnetic Susceptibilities," Oxford University Press, New York, N. Y., 1932; (b) see ref 24d, Chapter 1; (c) H. G. Hecht, "Magnetic Resonance Spectroscopy," Wiley, New York, N. Y., 1967, pp 38–39.

(31) T. K. Rebane, *Acad. Sci. USSR*, 46 (1960).

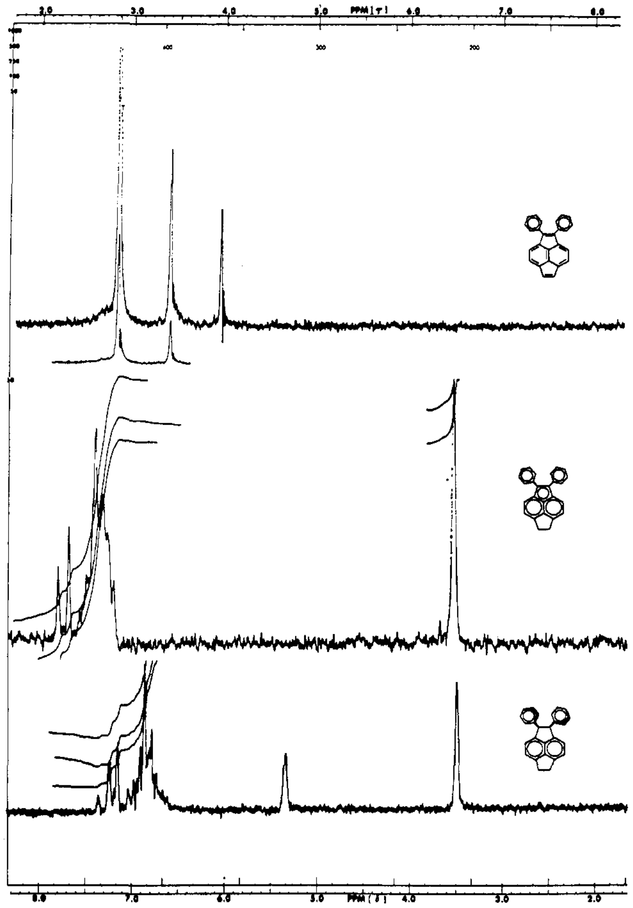

Figure 1. Nmr spectra of 1,2-diphenylpyracylene and its derivatives.

planar with the rest of the system. The absorptions for the phenyl rings shift back to the normal aromatic region and stretch from 7.2 to 7.6. Merely completing the peripheral conjugation in now going to the pyracylene (which should not affect the relative orientation of the two rings with respect to one another) causes the entire phenyl region to shift upfield to δ 7.18 indicating that some protons (presumably the ortho phenyl protons) experience an upfield shift of almost 24 Hz. The most reasonable explanation suggests that these upfield shifts arise from net shielding due to the existence of a paramagnetic ring current in the pyracylene moiety.

Reduction Potentials. Polarographic reduction provides further characterization of this unusual unsaturated system. Table IV lists the data for two pyracylenes.

Table IV. Polarographic Reduction Potentials

Compd	Half-wave potentials[a]	
	First wave	Second wave
I	−1.056	−1.635
XI	−0.972	−1.498

[a] *Vs.* standard calomel electrode.

Each wave is a reversible one-electron process. The products of the first wave as the corresponding radical anions were confirmed through their electron spin resonance spectra.[32]

The energy liberated in the addition of an extra electron to a closed-shell molecule, yielding the anion radical, is defined as its electron affinity (EA).[33] The energy change associated with polarographic one-electron reduction of the molecule in solution consists of a solvation energy component and its EA. The solvation energies associated with such reductions show only minor variation despite significant changes in the size and shape of the hydrocarbons.[34] Therefore, a rather good, roughly linear correlation is observed between the first half-wave potential and the energy of the LV–MO.[28b] The correlation holds well, even with LV–MO energies determined by simple Hückel calculations.[33b] The correlation using Hückel LV–MO energies predicts a first half-wave at −0.924 ± 0.109 eV *vs.* the standard calomel electrode (sce) for a system acquiring an electron in a formerly vacant NB–MO in excellent agreement with the values in Table IV. Recently, the absolute electron affinities have been measured for a series of conjugated hydrocarbons.[34] The variation of the absolute EA values for these molecules is roughly linear with the corresponding first half-wave reduction potential.[35] This approximately linear correlation suggests pyracylene to have an absolute EA of about 1.55 eV.

Mass Spectra. The mass spectra of pyracylene, 1,2-dibromopyracylene, and 1,2-diphenylpyracylene show the molecular ions as the base peaks. All show reasonably intense doubly charged molecular ions at m/e 88 for I, 164 for XI, and 166, 167, and 168 for VII. The unusual facility for formation of doubly charged molecular ions may reflect the stability (aromaticity) of a ten-electron peripheral system in the dication. The major fragmentations are summarized in the Experimental Section. It is of some note that the mass spectrum of diphenylpyracylene is characterized by unusually facile loss of hydrogens from the molecular ion.

Ultraviolet Spectra. Table V provides a comparison of the ultraviolet spectra of the three pyracylenes. The "p band regions" of 1,2-diphenylpyracylene and 1,2-dibromopyracylene show a definite hypsochromic shift relative to the corresponding pyracylene absorptions. The resonance delocalization of electrons from the bromine atoms and the phenyl rings into the electron deficient pyracylene π systems is probably responsible

Table V. Ultraviolet Spectral Data

Compd	λ, nm (ϵ)
I	427, 408, 405, 385, 341, 332, 326, 218
VII	391 (1,450), 363 (13,800), 355 (8,320), 346 (15,100), 339 (9,120), 331 (10,200), 317 (5,750), 303 (3,230), 261 (7,590), 222 (53,700)
XI	548 (450), 418 (700), 393 (1,300), 371 (12,500), 353 (15,500), 338 (12,000), 291 (15,500), 242 (23,750), 217 (47,000)

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(32) (a) B. M. Trost, S. F. Nelsen, and D. R. Britelli, *Tetrahedron Lett.*, 3959 (1967); (b) B. M. Trost and S. F. Nelsen, unpublished observations.

(33) (a) See ref 2d, p 273; (b) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, pp 175–185.

(34) R. S. Becker and E. Chen, *J. Chem. Phys.*, **45**, 2403 (1966).

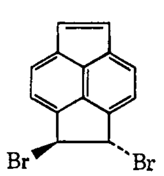
(35) A linear relation between the EA of a conjugated hydrocarbon and its first singlet transition energy has also been demonstrated; see R. S. Becker and W. E. Wentworth, *J. Amer. Chem. Soc.*, **85**, 2210 (1963).

for this shift. It is noteworthy that in proceeding from 1,2-dihydropyracylene to pyracylene, there is virtually no energy change in the p band region. A strong hypsochromic shift would have been observed if pyracylene was an aromatic system.[9]

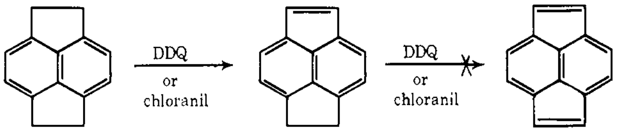
Conclusions

The application of a periphery electronic model for the 4*n* systems suggests a description of pyracylene as a perturbed [12]annulene. As such, it contradicts an earlier hypothesis that, according to Craig's rules, pyracylene should be an aromatic.[36] The available evidence clearly supports the former model.

The presence of a long-lived intermediate in the debromination of V provides support for considerably reduced stability associated with pyracylene as suggested by these considerations. Following the iodide promoted debromination by nmr shows the formation of a compound exhibiting an AB pattern with H_A at δ 7.96 and H_B at 7.06 (J_{AB} = 7 Hz) for 4 H, a singlet at 7.24 (2 H), and a singlet at 6.12 (2 H) in accord with structure XVI. The intermediacy of such a species strongly suggests that pyracylene is not much stabilized (if at all) relative to dihydropyracylene. Furthermore, 1,2-dihydropyracylene is readily formed by oxidation of pyracene with either 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil) or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). However, even the stronger of the two oxidizing agents, DDQ, fails to oxidize 1,2-dihydropyracylene to pyracylene—a fact which affords additional evidence that proceeding to the fully unsaturated system does not produce a significant increase (if any) in its stability.



XVI



Although aromatic character appears inconsistent with the properties of pyracylene, does the available evidence signify that pyracylene is a perturbed [12]-annulene? Its facile reduction correlating with the presence of an approximately nonbonding molecular orbital supports the contention. However, most indicative are the nmr spectral characteristics. The abnormal chemical shifts indicate a severe dampening of the usual diamagnetic ring currents. To the extent that the nature of the ring current is a valid criterion of electronic structure,[9a,29,30] pyracylene and its derivatives represent excellent examples of what a planar 4*n* system would look like. The chemical shifts are in fact at higher fields than either *s*-indacene,[9c] or even [12]-annulene.[4] In brief, the available data provide striking support for the peripheral electronic model describing pyracylene as a "pentalenoid" system.[37]

Experimental Section[38]

Preparation of Acenaphthene-5,6-dicarboxylic Acid Di-*N*,*N*-dimethylamide. A solution of 115 g (0.747 mmol) of acenaphthene in 400 ml of anhydrous chlorobenzene and 220 g (2.04 mol) of dimethylcarbamoyl chloride was prepared under nitrogen. The mixture was cooled to 0° and 277 g (2.07 mol) of aluminum chloride was added portionwise through a solid addition adapter. The mixture was then heated to 80° for 3 hr. At the end of this heating period, the deep purple solution was cooled to 0° and another 132 g (0.814 mol) of dimethylcarbamoyl chloride added. To this mixture was added 165 g (1.24 mol) of aluminum chloride and the solution refluxed 2 hr. The solution was cooled to 15° and poured into 4 l. of 5% aqueous hydrochloric acid precooled to 0°. This mixture was extracted into chloroform and the extracts were washed with water and aqueous sodium bicarbonate. After drying and removal of the solvent *in vacuo*, the resultant solid was recrystallized from ethanol-water to give 165 g (75% yield) of a white solid, mp 112–114°. Its infrared spectrum[39] showed a carbonyl absorption at 1625 cm^{-1} and aromatic absorption at 1607 cm^{-1}. The ultraviolet spectrum[40] exhibited λ_{max} (ϵ) at 305 (5750) and 322 nm (3630). The nmr spectrum[41] had proton absorptions for the *N*-methyl groups at 2.87 (s) and 3.09 (s), for the benzylic methylenes at 3.40 (s), and for the aromatic protons an AB pattern with δ_A at 7.37 and δ_B at 7.30 with J_{AB} = 7.0 Hz. Its mass spectrum exhibited a molecular ion peak at *m/e* 296 and abundant peaks at *m/e* 252, 250, 249, 219, 217, 216, 212, 210, and 152.

Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.9; H, 6.8; N, 9.4. Found: C, 73.0; H, 6.8; N, 9.4.

Preparation of Acenaphthene-5,6-dicarboxylic Acid. A suspension of 54.0 g (0.183 mol) of acenaphthene-5,6-dicarboxylic acid di-*N*,*N*-dimethylamide in 315 ml of concentrated hydrochloric acid was refluxed for about 1 hr. The mixture was cooled to 0° and then filtered. The solid was washed well with water. The resultant solid was dissolved by heating with 2.5 l. of 2 *N* aqueous sodium hydroxide. After decolorizing with Norit, the solution was cooled to 15° and acidified with concentrated hydrochloric acid. After drying overnight *in vacuo*, 37 g (84% yield) of dicarboxylic acid, mp 292–294° (lit.[21] mp 294°), was obtained.

Preparation of the Remaining Intermediates in Pyracene Preparation. The remaining intermediates were prepared by the method of Carpino and Gowecke.[21] The intermediates, melting points, and yields are as follows: dimethylacenaphthene 5,6-dicarboxylate (mp 171–177° (lit.[21] mp 171–177°), quantitative yield); 5,6-dihydroxymethylacenaphthene (mp 202–205° (lit.[21] mp 205–206°), 86% yield); 5,6-dibromomethylacenaphthene (mp 157–159° (lit.[21] mp 157–159°), 89% yield).

Preparation of Pyracene. A solution of 95 g (0.28 mol) of 5,6-dibromomethylacenaphthene in 410 ml of dry ether (distilled from lithium aluminum hydride) was prepared under nitrogen. A 388-ml sample of 2 *M* phenyllithium (0.776 mol) in benzene–ether was added dropwise over a 1.5-hr period. After stirring at 25° for 22 hr, the mixture was refluxed 4 hr. The solution was subsequently cooled and then quenched with 100 ml of water. The organic layer was further diluted with benzene and then washed well with water. After drying and evaporation of solvent *in vacuo*, 106.7 g of crude pyracene badly contaminated with biphenyl was obtained. Fractional vacuum sublimation at 0.1 mm and a temperature range of 25–125° removed the biphenyl impurity. The sublimation residue (84.8 g) was digested with 140 ml of acetone. After cooling, the light tan precipitate was filtered and dried to yield 50 g, mp 180–200°. This material was satisfactory for further work. Further purification by recrystallization from 1,2-dimethoxyethane–water produced colorless needles, mp 210–214° (lit.[21] mp 214–217°).

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(36) See ref 33b, pp 290–294.

(37) For development of the periphery electronic model for 4*n* + 2 peripheries, see J. R. Platt, *J. Chem. Phys.*, **22**, 1448 (1954).

(38) Melting points were taken on a Thomas-Hoover melting point apparatus and are corrected. Infrared spectra were determined on a Beckman IR-8 spectrophotometer, and ultraviolet spectra were recorded on Cary Model 11 and Model 15 spectrophotometers. Nmr spectra were determined on a Varian Associates Model A-60A spectrometer fitted with a variable-temperature probe. Chemical shifts are given in parts per million relative to TMS as an internal standard. Mass spectra were taken on a CEC 103 C or a MS-902 mass spectrometer at an ionizing current of 40 mA and ionizing voltage of 70 V. Analyses were performed by Spang Microanalytical Laboratory and MicroTech Laboratories, Inc. Unless otherwise indicated, extractions were performed with chloroform and magnesium sulfate was employed as a drying agent.

(39) Determined as a solution in chloroform.

(40) Determined as a solution in ethanol.

(41) Determined as a solution in deuteriochloroform.

Preparation of 1,2,5,6-Tetrabromopyracene.[42] A solution of 1.00 g (5.55 mmol) of pyracene in 1.3 l. of dry carbon tetrachloride was prepared under nitrogen. With a nitrogen stream passing through the system and a 500-W light bulb turned on, 3.60 g (22.5 mmol) of bromine in 40 ml of dry carbon tetrachloride was added by syringe through a Teflon capillary tubing directly into the solution with vigorous stirring. Upon completion of the bromine addition (approximately 30 min), 250 ml of water was added followed by 40 g of sodium thiosulfate and then 25 g of sodium bicarbonate. The organic layer was separated, dried, and evaporated *in vacuo* to produce 2.09 g of orange gum. An nmr spectrum suggested the gum to be a 3:2 mixture of 1,2,5,6-tetrabromopyracene and 1,2-dehydro-1,2,5,6-tetrabromopyracene. A pure sample of 1,2,-5,6-tetrabromopyracene could be obtained by fractional recrystallization from chloroform–methanol very inefficiently. The resultant tetrabromide was an off-white powder, mp 192–205° dec. The nmr spectrum[41] showed two singlets of equal intensity at δ 5.98 and 7.62. Its ultraviolet spectrum[40] had λ_{max} nm (ϵ) at 232 (47,900), 318 (12,000), and 332 (9330). Its mass spectrum showed no molecular ion but exhibited intense peaks at m/e 176 and 88.

Anal. Calcd for $C_{14}H_8Br_4$: C, 33.9; H, 1.6; Br, 64.5. Found: C, 34.0; H, 1.7; Br, 64.4.

For practical purposes, fractional recrystallization failed to provide pure 1,2,5,6-tetrabromopyracene. The separation of the two tetrabromides was finally achieved by derivatizing the unsaturated tetrabromide in the presence of the saturated tetrabromide. A typical example of this chemical purification scheme follows. A 1.00-g sample of the orange oil was refluxed with 4.0 g (14.8 mmol) of 1,3-diphenylisobenzofuran in 12.0 ml of carbon tetrachloride for 18 hr. Following removal of solvent *in vacuo*, the residue was stirred with 4.0 g (40.7 mmol) of maleic anhydride in 10.0 ml of benzene for 1.0 hr. The benzene solvent was removed *in vacuo*, the residue mixed with 100 ml of carbon tetrachloride, and the resultant slurry applied to 4 × 40 cm column prepared with a slurry of Florisil in carbon tetrachloride. Elution with carbon tetrachloride yielded all the desired 1,2,5,6-tetrabromopyracene in the first 500 ml of solvent. Evaporation *in vacuo* and trituration with 2–3 ml of carbon tetrachloride afforded a heavy precipitate of light yellow crystalline tetrabromide. Recrystallization from carbon tetrachloride yielded 242 mg of a first crop and 27 mg of a second crop of the desired compound (20% yield), mp 192–205° dec.

The Diels–Alder adduct of 1,3-diphenylisobenzofuran and 1,2-dehydro-1,2,5,6-tetrabromopyracene was isolated by elution with carbon tetrachloride from an alumina column and by subsequent recrystallization from ether–absolute ethanol to produce a pale yellow crystalline solid, mp 218–220° dec. The nmr spectrum[39] exhibited a multiplet at δ 7.8–8.2 (4 H), a multiplet at 7.0–7.77 (10 H), an AB pattern with δ_A at 7.14 and δ_B at 6.64 (J_{AB} = 7 Hz), and a singlet at 5.78. The ultraviolet spectrum[43] showed λ_{max} nm (ϵ) at 313 (12,610) and 333 (10,270).

Preparation of 5,6-Dihydro-1,2,5,6-tetrabromopyracylene. A 100-mg (0.555 mmol) sample of pyracene in 20 ml of dry carbon tetrachloride was refluxed on a steam bath for 16 hr with 1.20 g (6.74 mmol) of *N*-bromosuccinimide. At the end of this period, the mixture was cooled to room temperature and the succinimide removed by filtration. The filtrate was taken up with chloroform and extracted twice with equal volumes of 10% aqueous sodium bisulfite. After drying and evaporation of solvent, 146 mg (56% yield) of orange solid was obtained. Recrystallization from methanol produced orange crystals, mp 178–180°, of 5,6-dihydro-1,2,5,6-tetrabromopyracylene. The nmr spectrum[41] exhibited an aromatic AB pattern for 4 H with δ_A at 7.78 and δ_B at 7.60 (J_{AB} = 7 Hz) and a singlet for 2 H at δ 5.94. The ultraviolet spectrum[40] exhibited λ_{max} nm (log ϵ) at 368 (3.95), 352 (4.09), 335 (4.16), and 225 (4.78).

Anal. Calcd for $C_{14}H_6Br_4$: C, 34.1; H, 1.2; Br, 64.7. Found: C, 34.1; H, 1.3; Br, 64.8.

Preparation of Pyracylene and 1,2-Dibromopyracylene. A solution of 100 mg (0.20 mmol) of 1,2,5,6-tetrabromopyracene in 40 ml of acetone was refluxed in the presence of suspended powdered potassium iodide (2 g) and sodium thiosulfate pentahydrate (2 g) for 8 hr. During this time, the light yellow solution became deep reddish orange. After cooling to room temperature, suction filtration removed the inorganic precipitate which was washed with 50 ml of fresh acetone. The acetone solution was employed for further reactions or the pyracylene transferred to a different solvent. For transfer to a water-immiscible solvent, approximately 200 ml of the desired solvent (carbon tetrachloride, ether, or ethyl acetate) was added to the pyracylene–acetone solution and the mixture washed with six to eight 250-ml portions of water to remove acetone. The resultant solution was then dried with magnesium sulfate and concentrated *in vacuo* to the desired concentration. For transfer to a water-miscible solvent such as tetrahydrofuran or dioxane, the pyracylene was first transferred to ether. The ether was carefully evaporated to near dryness being careful not to allow any pyracylene to become completely solvent free. The deep reddish concentrate was immediately taken up in the new solvent. This procedure was repeated several times. The nmr[44] and ultraviolet[40] spectra are discussed in Results and Discussion. Its mass spectrum showed a molecular ion at m/e 176 as well as abundant ions at 150 and 88. Similar treatment of 5,6-dihydro-1,2,5,6-tetrabromopyracylene generated 1,2-dibromopyracylene whose spectral properties are summarized in Results and Discussion. Its mass spectrum exhibits molecular ion peaks at 336, 334, 332 as well as abundant peaks at 255, 253, 174, 168, 167, and 166.

Hydrogenation of Pyracylene. A 100-mg (0.20 mmol) sample of 1,2,5,6-tetrabromopyracene was converted to pyracylene as described above. After transfer to 20 ml of ethyl acetate, the deep reddish orange solution was hydrogenated at 1 atm and 25° over platinum oxide. The solution became colorless. After filtering through a mat of filter cel, the solvent was evaporated. Elution through a silica gel column with chloroform produced 35 mg (95% yield based on starting tetrabromide) of white solid, mp 204–214° (lit.[21] mp 214–217°), whose nmr and infrared spectrum were identical with an authentic sample of pyracene.

Preparation of 1,2-Diphenyl-1,2-dihydroxypyracene. From 13.01 g (62.6 mmol) of 1,2-diketopyracene,[18,45] 54.0 g (350 mmol) of bromobenzene, and 9.50 g (360 mmol) of magnesium turnings, there was obtained 17.42 g (79% yield) of crude light yellow solid, mp 176–178°, by the method of Richter and Feist.[24] After recrystallization from ethanol–water, 16.6 g (76% yield) of off-white solid, mp 180–181° (lit.[24] mp 179–181°), was obtained. Its infrared spectrum[39] shows only unassociated hydroxyl absorption at 3665 cm^{-1} indicative of the trans configuration. The ultraviolet spectrum[40] exhibits maxima, λ nm (ϵ), at 325 (2130), 313 (6960), 307 (7830), 229 (11,400), 295 sh (10,263), 287 (9517), 277 sh (6552), 233 (56,908), 227 (37,749), and 216 (31,570). The nmr spectrum[41] exhibits a pseudosinglet at δ 7.32 for all the aromatic hydrogens, a singlet for the benzyllic protons at 3.55, and a singlet at 2.15 for the hydroxyl protons.

Preparation of Diphosphorus Tetraiodide. Following the procedure of Germann and Taxler,[25] 16.0 g (0.516 mol) of white phosphorus and 130.88 g (0.516 mol) of iodine generated 101.78 g (73.0% yield) of diphosphorus tetraiodide, mp 122–123° (lit.[25] mp 124.5°).

Preparation of 1,2-Diphenyl-5,6-dihydropyracylene. A solution of 16.51 g (0.045 mol) of 1,2-diphenyl-1,2-dihydroxypyracene in 200 ml of dry ether was prepared under nitrogen. A solution of 17.5 g (0.034 mol) of diphosphorus tetraiodide in 1100 ml of ether was added portionwise over a 1.5-hr period. After 1 additional hr of stirring, the ether layer was washed with 1 l. of 1.0 *N* sodium hydroxide followed by 1 l. of sodium thiosulfate. After drying and evaporation *in vacuo*, 11.51 g of dark orange solid was obtained. The crude material was purified by passing it through a silica gel column and eluting with 5% benzene in hexane. Recrystallization of the orange band eluted first from the column from acetone–water produced 10.15 g (96% yield) of bright orange needles, mp 220–223° (lit.[24] mp 226–227°). Its ultraviolet spectrum[40] exhibited maxima, λ nm (ϵ) at 372 sh (10,779), 357 (13,356), 333 (11,947), 319 sh (7202), and 246 (63,832). Its nmr spectrum[39] appears in Results and Discussion.

Preparation of 1,2-Diphenyl-5,6-dihydro-5,6-dibromopyracylene. A 125-mg (0.379 mmol) sample of 1,2-diphenyl-5,6-dihydropyracylene, 81 mg of anhydrous sodium carbonate, 138 mg (0.775 mmol) of *N*-bromosuccinimide, and a trace of dibenzoyl peroxide were taken up with 20 ml of dry carbon tetrachloride under nitrogen. The orange solution was refluxed 1.5 hr and then cooled in an ice–methanol bath for 0.5 hr. Removal of the precipitated succinimide followed by evaporation of the solvent *in vacuo* produced 184 mg (100% yield) of red dibromide, mp 177–180°. Recrystallization from hexane generated 178 mg (97% yield) of red needles, mp 195–197°. Its ultraviolet spectrum[40] exhibited maxima, λ nm (ϵ) at

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(42) B. M. Trost and D. Brittelli, *J. Org. Chem.*, **32**, 2620 (1967).

(43) Determined as a solution in ether.

(44) Determined as a solution in carbon tetrachloride.

(45) H. J. Richter and F. B. Stocker, *J. Org. Chem.*, **24**, 366 (1959).

365 sh (9962), 354 (12,326), 341 (12,208), and 242 (37,165). Its nmr spectrum[39] exhibited an AB pattern for 4 H with δ_A at 7.78 and δ_B at 7.50 (J = 7.1 Hz), a multiplet for 10 H between 7.1 and 7.5, and a singlet for 2 H at 5.97.

Anal. Calcd for $C_{26}H_{16}Br_2$: C, 64.0; H, 3.3; Br, 32.7. Found: C, 63.7; H, 3.4; Br, 32.6.

Preparation of 1,2-Diphenylpyracylene. A solution of 184 mg (0.377 mmol) of 1,2-diphenyl-5,6-dihydro-5,6-dibromopyracylene in 40 ml of acetone was refluxed with a suspension of 1.8 g of powdered potassium iodide and 1.8 g of powdered sodium thiosulfate in the dark under nitrogen. After 5 hr reflux the solution was cooled to room temperature and the inorganic salts were removed by filtration. Dilution with 50 ml of water and extraction with ether gave an almost black ethereal layer. After drying and evaporation *in vacuo*, the deep green solid was immediately dissolved in a new solvent. Its ultraviolet[43] and nmr[44] spectral properties are summarized in Results and Discussion. Evaporation of solvent generated a deep green unstable compound which rapidly decomposed. Its mass spectrum showed a molecular ion at *m/e* 328 as well as abundant ions at 327, 326, 325, 324, 300, 164, and 150.

Anal. Calcd for $C_{26}H_{16}$: 328.1252. Found: 328.1254.

Bromine Addition to Pyracylenes. In an nmr tube, a solution of pyracylene in 0.2 ml of carbon tetrachloride generated from 24.8 mg (0.05 mmol) of tetrabromide was prepared under nitrogen. Bromine was added until the disappearance of the red-orange color at which time the nmr spectrum was identical with the starting tetrabromide. Comparison of the infrared spectra also demonstrated identicity. Evaporation of solvent and trituration with cold methanol gave 21.5 mg (87% yield) of colorless saturated tetrabromide. A similar experiment with 1,2-diphenylpyracylene and 1,2-dibromopyracylene generated 1,2-diphenyl-5,6-dibromo-5,6-dihydropyracylene and 1,2,5,6-tetrabromo-5,6-dihydropyracylene, respectively, identical in both nmr and infrared spectra with authentic samples.

Preparation of 1,2-Diphenyl-*cis*-5,6-dideuterio-5,6-dihydropyracylene. A solution of 1,2-diphenylpyracylene in 5 ml of dry 1,2-dimethoxyethane (freshly distilled first from potassium and then from lithium aluminum hydride) was prepared under nitrogen as previously described starting from 140 mg (0.427 mmol) of 1,2-diphenyl-5,6-dihydropyracylene. The solution was diluted with an equal volume of methanol-d_1 and then 120 mg (0.652 mmol) of dipotassium azodicarboxylate[46] added. The latter salt had previously been washed thoroughly with ten portions of cold methanol to remove occluded potassium hydroxide followed by drying *in vacuo* for at least 48 hr. To the resulting suspension, 0.120 ml of deuterioacetic acid was added very slowly. After stirring for 0.5 hr, addition of dipotassium azodicarboxylate followed by deuterioacetic acid was repeated five times. The resulting red solution was then poured into cold 10% aqueous sodium bisulfite and extracted with ether. After drying and evaporation, the product was passed through a silica gel column utilizing 5% benzene in hexane. The first orange band contained 102 mg (73% yield), mp 218–219°, of orange crystals. Mass spectral analysis at 12 eV indicated 94.2% d_2 and 5.8% d_1. The nmr spectrum[44] was identical with the perhydro material except for the diminishment of the signal for the benzylic protons. Infrared analysis[44] showed C–D stretching vibrations at (cm^{-1}) 2195, 2180, and 2165.

Determination of Stereochemistry of Bromination. Dibromination of 20 mg (0.060 mmol) of 1,2-diphenyl-5,6-*cis*-dideuterio-5,6-dihydropyracylene (94.2% d_2, 5.8% d_1) was carried out as described above using 22 mg of *N*-bromosuccinimide in 10 ml of dry carbon tetrachloride to produce 30 mg (quantitative yield) of red dibromide, mp 177–178°. Reductive elimination of the bromines with iodide ion followed by reduction utilizing diimide generated from 93.0 mg (0.505 mmol) of dipotassium azodicarboxylate and 28.9 mg of acetic acid was performed as detailed above. Subsequent column chromatography on silica gel with 10% benzene in hexane produced 13 mg (65% yield) of dihydropyracylene containing varying deuterium content. Mass spectral analysis at 12 eV indicated the material contained 13.6% d_0, 47.0% d_1, and 39.4% d_2.

Determination of Isotope Effect. A solution of 50 mg (0.151 mmol) of 1,2-diphenyl-*cis*-5,6-dideuterio-5,6-dihydropyracylene (36.4% d_2, 49.1% d_1, and 14.5% d_0) in 10 ml of dry carbon tetrachloride was refluxed for 1 hr in the presence of 27 mg (0.151 mmol) of *N*-bromosuccinimide containing a trace of dibenzoyl peroxide. The succinimide was removed by filtration and the solvent removed by evaporation *in vacuo* to yield 62 g (quantitative yield), mp 230°, of monobromide with mixed deuterium content. The nmr spectrum[44] showed the aromatic protons between 7.15 and 7.90, the methine benzyllic proton at 5.75–5.90, and the methylene protons at 4.78. This material was dissolved in 10 ml of *tert*-butyl alcohol and subsequently added to 40 ml of 1 *N* potassium *tert*-butoxide in *tert*-butyl alcohol. After stirring at room temperature for 1 hr, the solution was poured into 300 ml of ice water and extracted with ether. After drying and concentration *in vacuo*, the deep green solid was converted back to 5,6-dihydro material utilizing diimide as detailed above. After column chromatography, 36.7 mg (73.5% yield), of bright orange solid, mp 215–217°, was obtained. Mass spectral analysis at 12 eV indicated a deuterium distribution of 35.0% d_0, 52.6% d_1, and 12.4% d_2.

Preparation of 1,2-Dihydropyracylene. A solution of 500 mg (2.78 mmol) of pyracene and 630 mg (2.78 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 10 ml of dry benzene was refluxed 24 hr under nitrogen. After dilution with 200 ml of ether, the ethereal layer was washed with cold 10% aqueous sodium hydroxide until the washings were no longer yellow. The solution was subsequently dried and evaporated *in vacuo*. The residue was chromatographed on Fisher alumina with benzene as the eluting solvent to produce 210 mg (42% yield) of yellow crystals, mp 156–157° (lit.[17] mp 155–156°). It was recrystallized from ether-hexane. Its ultraviolet spectrum[40] showed λ_{max} nm (ϵ) at 358 (5261), 352 sh (5151), 343 (7398), 327 (6521), 321 (8659), 315 sh (5645), 308 (4439), and 240 (41,430). Its nmr spectrum[44] is summarized in Results and Discussion. Its mass spectrum shows a molecular ion at *m/e* 178 (base peak) and intense peaks at 177, 176, 152, 151, 150, and 88.

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(46) Obtained by potassium hydroxide hydrolysis of azodicarbonamide. For leading references, see S. Hünig, H. R. Müller, and W. Thies, *Angew. Chem., Int. Ed. Engl.*, **4**, 271 (1965).