Lumichrome is another dye which is structurally similar to riboflavin but has a higher energy triplet state[8] and is a poorer hydrogen abstractor in its excited state than is riboflavin.[9] With lumichrome as the sensitizer and a relatively high concentration of I (10^{-2} *M*), an enone:epoxy ketone ratio of 5.5:1 was obtained. This represents a sixfold change in the product distribution as compared with riboflavin and therefore tends to confirm our interpretation of the riboflavin data and support the "two singlet oxygen" hypothesis.[10]

In view of the demonstrated ability of excited dye molecules to abstract hydrogen atoms from good donors such as phenol,[11] it was possible that enone III production might also be due to hydrogen-atom abstraction by the excited dye molecules. If hydrogen abstraction from I by the excited dye were important in the formation of III, the excited dye would have two competing reaction paths: hydrogen abstraction from I and transfer of energy to oxygen. In this case, the product distribution should be oxygen concentration dependent. This possibility is eliminated with eosin, for example, by the observation that there was no change in the product distribution when the oxygen pressure was varied from 0.2 to 10 atm.[12]

The observed dependence of the enone:epoxy ketone ratio on both the substrate concentration and the sensitizer triplet-state energy is perfectly in accord with the proposed involvement of ${}^1\Sigma_g{}^+$ and ${}^1\Delta_g$ oxygen molecules as intermediates in the sensitized photooxygenation of I. These results do not appear to be consistent with the involvement of some of the other species which have been suggested as intermediates in sensitized photooxygenation reactions.[13,14]

(8) R. W. Chambers and D. R. Kearns, unpublished results.

(9) B. te Nijenhuis and W. Berends, *Photochem. Photobiol.*, **6**, 491 (1967).

(10) The fact that the enone:epoxy ketone ratio was 5.5:1 rather than 3:1 may possibly be due to a small contribution from hydrogen-abstraction reactions.

(11) L. I. Grossweiner and E. F. Zwicker, *J. Chem. Phys.*, **34**, 1411 (1961).

(12) This conclusion is further supported by the results obtained using triphenylene as the sensitizer.[2] Triphenylene (E_t = 67 kcal) should be much less susceptible to photoreduction than any of the other dyes which were used, and yet when used as a sensitizer it still gave the 3:1 enone:epoxy ketone ratio expected for a high-energy sensitizer.

(13) K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964).

(14) G. O. Schenck, *Naturwissenschaften*, **40**, 205, 229 (1953).

(15) Alfred P. Sloan Fellow.

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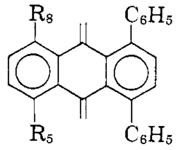
Crowded Anthracenes. I. 1,4,5,8-Tetraphenyl- and 1,4-Diphenyl-9,10-dimethylene-9,10-dihydroanthracene

Sir:

Molecular orbital calculations indicate that quinodimethanes, which lack substituents on the methylene groups, possess unusually high free valence at the terminal carbon atoms.[1] In agreement with these predictions compounds such as *p*-xylylene[2] and 9,10-dimethylene-9,10-dihydroanthracene[3-5] are highly reactive, and ordinary synthetic routes to this type of quinodimethane invariably yield cyclodimer and/or polymer. During a study of the effects of nonbonded aryl groups on the physical and chemical properties of adjacent functionalities we have discovered a set of anthraquinodimethanes that are kinetically stable despite the absence of substituents on the methylene groups. We now wish to report the synthesis of two of these compounds, **1** and **2**.



1, $R_5 = R_8 = C_6H_5$
2, $R_5 = R_8 = H$

Addition of methyllithium to 1,4,5,8-tetraphenylanthraquinone[6] gave the corresponding diol,[7,8] mp 309–312° dec. Treatment of this diol with hydriodic acid in benzene–methanol at 10–30° gave colorless, crystalline **1** in a yield of 80%, $C_{40}H_{28}$, mp 277–278.5° dec, mol wt 489 (isopiestic), and *m/e* 508, $\nu_{max}^{CS_2}$ 3025, 910 (C=CH$_2$), $\lambda_{max}^{C_6H_{12}}$ mμ (log ϵ) 229 (4.78) and 273 (4.52), nmr (CDCl$_3$, internal TMS) δ 4.84 (singlet, four methylene protons), δ 7.2–7.6 (multiplet, 24 aromatic protons). Furthermore, both the position and the shape of the peak at δ 4.84 are unchanged over the temperature range of -20 to 200°. The dipole moment of **1**, measured in benzene, amounted to 0.44 ± 0.05 D.

Similarly, addition of methyllithium to 1,4-diphenylanthraquinone[6] gave the diol,[8] mp 167–169°, and treatment with aqueous hydrochloric acid in dioxane gave, after column chromatography, colorless crystalline **2** in a yield of 52%, $C_{28}H_{20}$, mp 162–164° dec, *m/e* 356, $\nu_{max}^{CS_2}$ 3050, 907 (C=CH$_2$), $\lambda_{max}^{C_6H_{12}}$ mμ (log ϵ) 223 (4.65), 233 s (4.56), and 273 (4.49), nmr (CCl$_4$, internal TMS) δ 4.80 (broad singlet, two methylene protons), δ 5.35 (broad singlet, two methylene protons), δ 7.0–7.5 (multiplet, 16 aromatic protons).

The ultraviolet maxima at 273 mμ exhibited by both **1** and **2** are presumably due to the anthraquinodimethane chromophore and are in excellent agreement with the value of 275 mμ predicted by Pullman and coworkers for the unsubstituted hydrocarbon, 9,10-dimethylene-9,10-dihydroanthracene.[9,10]

A nonzero dipole moment for **1** confirms a "boat" or "butterfly" geometry for this quinodimethane and simplifies the interpretation of the nmr spectrum.[11] In this connection a variable-temperature nmr study by Curtin and co-workers has revealed that 10,10-dimethyl-9-methylene-9,10-dihydroanthracene exhibits

(1) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," W. H. Freeman and Co., San Francisco, Calif., 1965, pp 103–120.

(2) The chemistry of *p*-xylylene and its polymers has been reviewed by L. A. Errede and M. Szwarc, *Quart. Rev.* (London), **12**, 301 (1958).

(3) G. Rio, *Ann. Chim.* (Paris), **9**, 229 (1954).

(4) P. Tardieu, *Compt. Rend.*, **248**, 2885 (1959).

(5) J. H. Golden, *J. Chem. Soc.*, 3741 (1961).

(6) E. Bergmann, L. Haskelberg, and F. Bergmann, *J .Org. Chem.*, **7**, 303 (1942).

(7) All new compounds gave satisfactory elemental analyses.

(8) The ultraviolet, infrared, and nmr spectra of this compound are consistent with the assigned structure.

(9) A. Pullman, B. Pullman, E. D. Bergmann, G. Berthier, E. Fischer, D. Ginsburg, and Y. Hirshberg, *Bull. Soc. Chim. France*, 707 (1951).

(10) This hydrocarbon has been reported by Tardieu[4] to absorb at 283 mμ in ethyl ether at -25°.

(11) Although theoretical treatments assume a planar structure, nothing is known concerning the geometry of the parent hydrocarbon 9,10-dimethylene-9,10-dihydroanthracene.

rapid interconversion between "boat" conformers at room temperature[12] and that the vinyl protons in this compound exhibit a chemical shift of δ 5.60 (CCl_4).[13] Thus the methylene protons in **1** are shielded, relative to this model, by 0.76 ppm by the adjacent pairs of nonbonded phenyl groups. However, one set of vinyl protons in the diphenyl derivative **2** is more shielded (0.80 ppm), relative to the same model compound, by single phenyl groups. This observation must reflect a somewhat different geometry for **1** and **2**.

The chemical properties of these anthraquinodimethanes are consistent with the assignments of structure. For example, catalytic hydrogenation of **2** gave 1,4-diphenyl-9,10-dimethylanthracene, $C_{28}H_{22}$, mp 215–217.5°, $\lambda_{max}^{C_6H_{12}}$ mμ (log ε) 2.79 (4.80), 414 (4.02), 430 s (3.95), nmr (C_6D_6, internal TMS) δ 2.48 (singlet, six methyl protons), δ 7.1–8.1 (multiplet, 16 aromatic protons). Similar treatment of **1** furnished a mixture of 1,4,5,8-tetraphenyl-9,10-dimethylanthracene and its methylene tautomer. The characterization and the results of equilibration studies of these compounds and applications to problems of long-range magnetic shielding are given in the accompanying communication.[14]

The kinetic stability of **1** and, particularly, **2** is rather surprising in view of consistent failure to isolate the parent hydrocarbon. Although **1** and **2** appear routinely stable in the solid state, both exhibit some instability in solution. For example, reflux of dilute solutions of these compounds in isooctane for 17 hr under nitrogen leads to the formation of small amounts of yellow product or products with anthracene-like ultraviolet absorption. The diphenyl derivative **2** is less stable than **1** under these conditions and is actually quite labile in concentrated solution. Although little is known about the mechanism of cyclodimerization or polymerization of 9,10-dimethylene-9,10-dihydroanthracene,[15] it is certainly reasonable to ascribe the protective effect of the phenyl groups in **1** and **2** to steric hindrance to the bimolecular methylene–methylene interactions required for such reactions.

We are actively investigating the synthesis of other potentially stable quinodimethanes and the chemistry of **1** and **2**.[16]

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(12) D. Y. Curtin, C. G. Carlson, and C. G. McCarty, *Can. J. Chem.*, **42**, 565 (1964).

(13) Private communication from Professor Curtin.

(14) S. C. Dickerman and J. R. Haase, *J. Am. Chem. Soc.*, **89**, 5458 (1967).

(15) The polymerization of *p*-xylylene is believed to be self-induced; see ref 2.

(16) This work was supported in part by an Institutional Grant from the National Science Foundation.

(17) National Science Foundation Trainee, 1965–1967, and National Institutes of Health Predoctoral Fellow, 1967.

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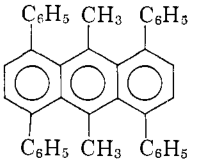
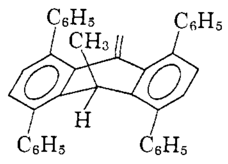
Crowded Anthracenes. II. Methylene–Methylarene Tautomerism and Long-Range Magnetic Shielding in 1,4,5,8-Tetraphenyl-9,10-dimethylanthracene

Sir:

We wish to report the synthesis of the crowded molecules 1,4,5,8-tetraphenyl-9,10-dimethylanthracene (**1**) and 1,4,5,8-tetraphenyl-10-methyl-9-methylene-9,10-dihydroanthracene (**2**) from 1,4,5,8-tetraphenyl-9,10-dimethylene-9,10-dihydroanthracene.[1] The results of equilibration studies are given, and applications to quantitative aspects of long-range magnetic shielding are discussed.



1



2

Catalytic hydrogenation of 1,4,5,8-tetraphenyl-9,10-dimethylene-9,10-dihydroanthracene[1] gave a mixture composed of about 34% **1** and 66% **2**. The combined solids were extracted and then recrystallized under nitrogen to yield the less soluble component, **1** ($C_{40}H_{30}$,[2] mp 363–367° dec, *m/e* 510, $\lambda_{max}^{C_6H_{12}}$ mμ (log ε) 224 (4.86), 285 s (4.88), 291 (4.98), 407 s (3.91), 429 (4.16), and 454 (4.19), nmr (130° in C_6D_6, internal TMS) δ 1.77 (singlet, six methyl protons), 7.0–7.6 (multiplet, 24 aromatic protons). Column chromatography of the hydrogenation mixture furnished **2**, $C_{40}H_{30}$, mp 212.5–214°, *m/e* 510, $\lambda_{max}^{C_6H_{12}}$ mμ (log ε) 250 (4.76), nmr ($CDCl_3$, internal TMS) δ 1.00 (doublet, three methyl protons), 4.57 (quartet, one tertiary proton), 4.91 (singlet, two vinyl protons), 7.1–7.7 (multiplet, 24 aromatic protons), and the 9,10-photooxide of **1** (mp 257–259° dec).[3] The methyl group in **2** is assigned an axial position on the basis of the observed nmr spectrum and comparison of chemical shifts in reference compounds.

Given the nmr spectra of **1** and 1,4-diphenyl-9,10-dimethylanthracene,[1] it is now possible to make a quantitative evaluation of the long-range magnetic shielding due to two and one nonbonded phenyl group(s), respectively. Since the methyl protons in 9,10-dimethylanthracene exhibit a chemical shift of δ 3.08 in deuteriochloroform, the shielding amounts to 1.31 and 0.60 ppm, respectively.[4] Although a value of 1.3 ppm appears to be among the largest yet reported, it is far less than that calculated for **1** (4.7 ppm) using the theoretical model of Johnson and Bovey.[5] Similar discrepancies between theory and experiment have been reported recently by Regan and Miller for a series of polyphenyldialkylbenzenes, 9-phenyl-1,4-dimethylanthracene, and several 2,3,9-triphenyl-1,4-dialkylanthracenes.[6,7] Although some of these differences may be attributed to steric distortions, the major part of the discrepancy appears to arise from an overestimate of

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(1) S. C. Dickerman, J. H. Berg, J. R. Haase, and R. Varma, *J. Am. Chem. Soc.*, **89**, 5457 (1967).

(2) All new compounds gave satisfactory elemental analyses.

(3) The ultraviolet, infrared, and nmr spectra of this compound are consistent with the assigned structure.

(4) The low solubility of **1** prevented direct comparison of chemical shifts in carbon tetrachloride or deuteriochloroform. Nevertheless, the comparison between the reference compound in deuteriochloroform and the others in perdeuteriobenzene is valid since the methyl groups in **1** are immune to solvent anisotropic effects and the correction for 1,4-diphenyl-9,10-dimethylanthracene increases the intramolecular shielding by only about 0.05 ppm: J. H. Haase, unpublished results.

(5) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(6) T. H. Regan and J. B. Miller, *J. Org. Chem.*, **32**, 592 (1967).

(7) Additional examples of compounds that exhibit less than "calculated" shielding are 1-phenyl-9-methyl-, 1,4-diphenyl-9-methyl-, 1-phenyl-9,10-dimethyl-, 9-*p*-methoxyphenyl-1,4-dimethyl-, 9-α-naphthyl-1,4-dimethyl-, and 9-β-naphthyl-1,4-dimethylanthracene: J. R. Haase, unpublished results.