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]

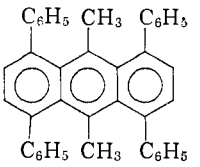
(12) D. Y. Curtin, C. G. Carlson, and C. G. McCarty, *Can. J. Chem.*, **42**, 565 (1964).
(13) Private communication from Professor Curtin.
(14) S. C. Dickerman and J. R. Haase, *J. Am. Chem. Soc.*, **89**, 5458 (1967).
(15) The polymerization of *p*-xylylene is believed to be self-induced; see ref 2.
(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.

S. Carlton Dickerman, Jeffrey H. Berg, Jan R. Haase,[17] Ravi Varma
Department of Chemistry, New York University
New York, New York 10453
Received July 19, 1967

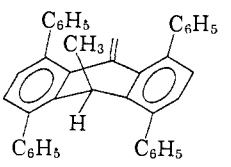
Crowded Anthracenes. II. Methylene–Methylarene Tautomerism and Long-Range Magnetic Shielding in 1,4,5,8-Tetraphenyl-9,10-dimethylanthracene

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

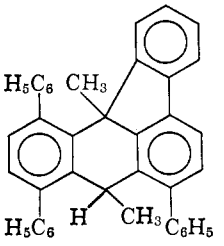
Catalytic hydrogenation of 1,4,5,8-tetraphenyl-9,10-dimethylene-9,10-dihydroanthracene[1] gave a mixture composed of about 34% **1** and 66% **2**. The combined solids were extracted and then recrystallized under nitrogen to yield the less soluble component, **1** ($C_{40}H_{30}$,[2] mp 363–367° dec, *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

(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.

ring current, as has been suggested by both Dailey[8] and Pople.[9]

Treatment of the mixture of **1** and **2**, obtained by hydrogenation, with trifluoroacetic acid gave the cyclization product **3**, mp 213–214°.[3,10] Although this



3

side reaction prevents a quantitative measure of the relative thermodynamic stabilities of **1** and **2**, it is clear from equilibration studies of the mixture and of **1** alone in benzene–trifluoroacetic acid that **2** is the more stable tautomer. Equilibration of **1** and the hydrogenation mixture of **1** and **2**, with 0.025 *M* sodium methoxide in DMSO containing 0.02 wt % methanol[11] at room temperature, gave mixtures composed of 0.30–0.35% **1** and 99.70–99.65% **2**. However, identical treatment of **2** failed to yield **1** in amounts that could be detected by ultraviolet spectroscopy. Therefore, the equilibrium constant for the reaction **1** $\rightleftarrows$ **2** has a minimum value of about 300, and $\Delta G \leq -3.4$ kcal/mole at room temperature. Since methylene–methylanthracene tautomerism of 1,4-diphenyl-9,10-dimethylanthracene has not been detected, the introduction of two additional phenyl groups into the 5,8 positions in this compound essentially reverses the usual pattern of thermodynamic stability.[12] The observation that **2** is the more stable tautomer must mean that the loss in delocalization energy is more than compensated by relief of steric compression. In this connection the crowded nature of **1** is almost self-evident. Thus, if **1** possesses a more or less normal geometry, the distance between the nodal planes of the **1** and **8** phenyl groups is about 4.8 A, in contrast to the 7.4 A represented by twice the sum of the van der Waals radii of a methyl and two phenyl groups.[13]

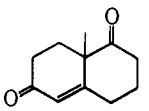
(8) B. P. Dailey, *J. Chem. Phys.*, **41**, 2304 (1964).
(9) J. A. Pople, *ibid.*, **41**, 2559 (1964).
(10) There is ample precedent for this type of reaction. For an example in the anthracene series, see C. Weizmann, E. Bergmann, and L. Haskelberg, *J. Chem. Soc.*, 391 (1939).
(11) E. C. Steiner and J. M. Gilbert, *J. Am. Chem. Soc.*, **87**, 382 (1965).
(12) There is no real precedent for this finding in that **1** appears to be the first example of a 1,4,5,8-tetrasubstituted 9,10-dimethylanthracene. However, 1,5-dichloro-9-methylene-10-methyl-9,10-dihydroanthracene was prepared many years ago under conditions that imply thermodynamic stability by E. deB. Barnett and J. W. Cook, *Ber.*, **61B**, 314 (1928); recently P. de Bruyn [*Bull. Soc. Chim. Belges.*, **69**, 328 (1960)] has reported the synthesis of 1,5-dichloro-9,10-dimethylanthracene and has shown that this is indeed the less stable tautomer. Furthermore, both 1,4-dimethoxy-9,10-dimethylanthracene and its methylene tautomer, as well as evidence that the former is the stable isomer, have been reported by Y. Lepage, *Compt. Rend.*, **246**, 954 (1958).
(13) Supported in part by an Institutional Grant from the National Science Foundation.
(14) National Science Foundation Trainee, 1965–1967, and National Institutes of Health Predoctoral Fellow, 1967.

S. Carlton Dickerman, Jan R. Haase[14]
Department of Chemistry, New York University
New York, New York 10453
Received July 19, 1967

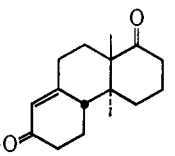
The Isoxazole Annelation Reaction. A Method for the Construction of Cyclohexenone Rings in Polycyclic Systems

Sir:

The annelation of ketones has engaged our attention for some time as we have sought a method of some generality which would serve, for instance, to transform the bicyclic dione I into the annelated tricyclic substance V. We started from the assumption that suitably



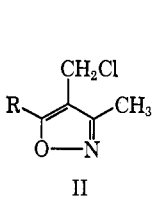
I



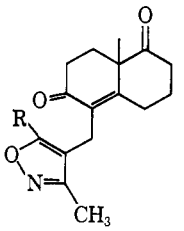
V

substituted 4-halomethylisoxazoles (*cf.* II) might be used in a new annelation method provided they could meet the following requirements: (a) they must be capable of monoalkylating α,β-unsaturated ketones (I → III); (b) the isoxazole ring must be able to survive chemical transformations in other parts of the molecule, such as hydrogenation (III → IV); (c) conditions must be found for the eventual transformation of the substituent into the desired new ring (IV → V).

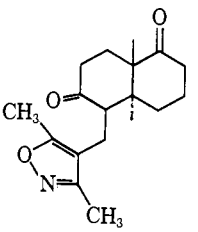
We now consider in a general way the problems involved in this scheme, while the application to the specific case of steroid syntheses is taken up in accompanying communications. We were encouraged to find that alkylation of the sodium enolate from 10-methyl-$\Delta^{1,9}$-octalin-2,5-dione (I)[1] (sodium hydride–glyme) with 3,4-dimethyl-4-chloromethylisoxazole[2] led to III, R = CH_3, mp 85–86°, λ_{max}^{EtOH} 252 mμ (ϵ 10,000), in 70% yield.[3]



II



III



IV

The transformation of III, R = CH_3, into IV put a severe requirement on the isoxazole ring because of its well-documented[4] lability to chemical or catalytic reduction. We found that hydrogenation with palladium–charcoal reduced the double bond considerably more rapidly than it cleaved the isoxazole ring in a variety of media. The desired *trans* stereochemistry was produced most selectively by using 3:1 ethyl acetate–triethylamine when IV, mp 164–165°,[3] was obtained in 70% yield.[5]

(1) S. Ramachandran and M. S. Newman, *Org. Syn.*, **41**, 38 (1961).
(2) N. K. Kochetkov, E. D. Khomutova, and M. V. Bazilevskii, *J. Gen. Chem. USSR*, 2762 (1958).
(3) Satisfactory analytical and spectra data were obtained for this substance.
(4) N. K. Kochetkov and S. D. Sokolov, *Advan. Heterocyclic Chem.*, **2**, 416 (1963).
(5) In a number of other cases which we have examined, hydrogenolysis of the isoxazole ring competes with hydrogenation at other points in the molecule. We have made the potentially important observation that the rate of hydrogenolysis of isoxazole rings is *dramatically affected by the pH of the medium.* For instance, although the isoxazole ring of the simple model VI, R = H, was completely hydrogenolyzed with palladium charcoal in 3 hr in 1:1 ethyl acetate–triethylamine, it was essentially unaffected in 5:1 ethyl acetate–acetic acid in 20 hr.