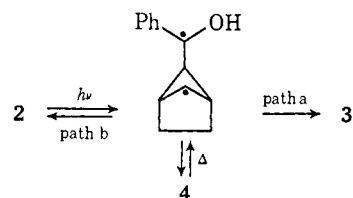


an AB quartet ($J = 10.0$ Hz) centered at τ 8.31. The strong upfield shift of H_2 (relative to H_6) can be attributed to long-range shielding by the π electrons of the phenyl ring.⁹ The H_1 - H_6 bridgehead-bridgehead long-range coupling in **4** was determined by the preparation of 7-phenyltricyclo[3.2.0.0^{2,6}]heptan-7-ol-1- d_1 (**5**) via the irradiation of *exo*-5-benzoylbicyclo[2.1.1]hexane-5-*endo*- d_1 (**6**).¹⁰

The nmr spectrum of the monodeuterated compound (**5**) showed a coupling constant of 2.70 Hz between the deuterium and the bridgehead hydrogen. Since hydrogen-hydrogen coupling is as great by a factor of 6.55 as deuterium-hydrogen coupling,¹¹ the value obtained is essentially identical with that encountered in the bicyclo[1.1.1]pentane system (*i.e.*, $J = 18.0$ Hz)^{12,13} indicating that the geometries of both ring systems are essentially the same.

Thermal decomposition of **4** at 150° afforded a mixture of **2** (33%) and **3** (67%). The formation of these products can best be accounted for by a thermal cleavage of the bridgehead C-C bond followed by ring opening of the diradical (path a) or by a 1,5-H transfer step (path b). The formation of **3** and **4** from the irradiation



of **2** may be considered to be analogous to the Norrish type II cleavage and cyclobutanol formation observed with the irradiation of aliphatic ketones containing γ -hydrogens.¹⁴ The behavior of the diradical generated by thermolysis of **4** is essentially the same as that encountered in the Norrish type II process and once again illustrates the reverse hydrogen transfer step of 1,4 diradicals.¹⁵⁻¹⁷

The quantum yield for disappearance of ketone ($\Phi = 0.06$) is considerably lower than that of related acyclic phenyl ketones¹⁸ and its value is not significantly enhanced with added *t*-butyl alcohol. The photolysis is readily quenched by the addition of piperylene, in agreement with a $n-\pi^*$ triplet as the reactive excited state. Since the quantum yield is independent of solvent, the low efficiency cannot be attributed to disproportionation of the 1,4 diradical.¹⁸ The low efficiency must be related instead to some molecular feature of **2** which re-

tards formation of the biradical and allows direct radiationless decay to compete with chemical reaction of the triplet. We suspect that the inefficiency of the photo-process is due to the unfavorable geometry required for internal hydrogen abstraction. The preferred transition state for internal hydrogen transfer is one in which carbon, hydrogen, and the nonbonding electron on oxygen can approximate a linear configuration.¹⁹ These stereoelectronic requirements cannot be readily met with the above ketone.

It is interesting, at this point, to compare the photo-efficiency of **2** with that of cyclobutyl phenyl ketone (**7**) ($\Phi = 0.03$). The cyclobutane ring is quite flexible and exhibits a dynamic ring-bending equilibrium which allows for conformation equilibration of monosubstituted cyclobutanes.²⁰ It was previously argued that one possible source of inefficiency in the cyclobutyl phenyl ketone system was the low concentration of the conformer having the benzoyl group in the pseudo-axial position.² Bicyclo ketone **2** is an appropriate model for the reactive conformer of **7**, since the benzoyl group is now locked into the axial position. If the inefficiency of **7** was totally due to the low population of the reactive conformer, then we would expect that **2** would be similar to valerophenone in terms of photo-efficiency.²¹ This is certainly not the case and suggests that the inefficiency of both **2** and **7** are related to the poor stereoelectronic features of these ketones.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant No. GP-9385).

(19) N. J. Turro and D. W. Weiss, *ibid.*, **90**, 2185 (1968).

(20) J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *ibid.*, **69**, 2483 (1947).

(21) It has been pointed out that the quantum efficiency of type II photoelimination is not directly related to triplet-state reactivity for phenyl ketones that undergo significant disproportionation from the 1,4 diradical.²² However, ketones **2** and **7** show no significant solvent effects and consequently it is assumed that quantum efficiency and triplet reactivity of these ketones are closely related.

(22) P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, **90**, 5896 (1968).

(23) Fellow of the Alfred P. Sloan Foundation, 1968-1970.

Albert Padwa,²³ Walter Eisenberg

Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

Received February 6, 1970

Dibenzopentalenyl Dianion. A Perturbed [12]Annulene Dianion

Sir:

Perturbation theory predicts that dibenzo[*cd,gh*]pentalene (**I**) should be an unusually good example of the periphery electronic model which describes this system as a perturbed [12]annulene.^{1a,b} SCF calculations² confirm this prediction; these calculations suggest that the first excited triplet state lies only 0.3 eV above the ground state! In this communication we wish to report the synthesis of the first derivative of this molecule, dilithium dibenzo[*cd,gh*]pentalenide (**II**). The properties of this derivative clearly support the periphery model as

(1) (a) B. M. Trost and G. M. Bright, *J. Amer. Chem. Soc.*, **89**, 4244 (1967), and references therein; (b) P. Kinson and B. M. Trost, *Tetrahedron Lett.*, 1075 (1969).

(2) We express our gratitude to Dr. Howard E. Simmons for carrying out a SCF-PPP calculation on this system.

(9) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p 125.

(10) The monodeuterated bicyclo ketone **6** was prepared from the photolysis of *syn*-7-chlorodiazonorcamphor in D_2O followed by removal of the 7-chloro substituent with lithium metal and conversion of the acid to the ketone with phenyllithium.

(11) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 188.

(12) K. B. Wiberg and D. S. Connor, *J. Amer. Chem. Soc.*, **88**, 4437 (1966).

(13) A. Padwa, E. Shefter, and E. Alexander, *ibid.*, **90**, 3717 (1968).

(14) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 154.

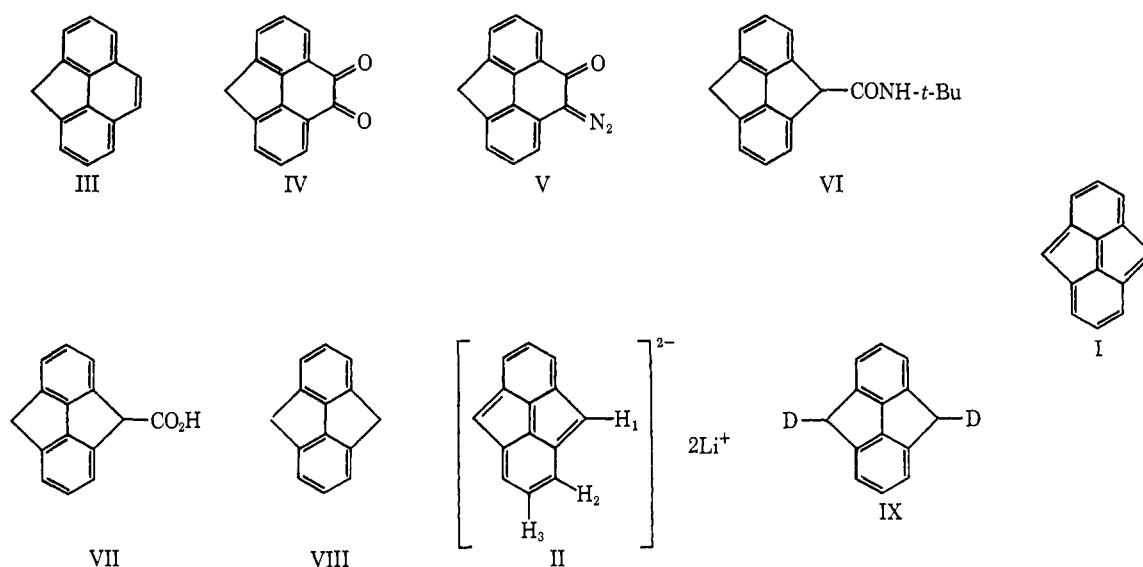
(15) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5898 (1967); *Tetrahedron Lett.*, 1753 (1967).

(16) A. Padwa and E. Alexander, *J. Amer. Chem. Soc.*, **90**, 6871 (1968).

(17) N. C. Yang, S. P. Elliott, and B. Kim, *ibid.*, **91**, 7551 (1969).

(18) P. J. Wagner and H. N. Schott, *ibid.*, **91**, 5383 (1969).

Chart I. Intermediates in the Synthesis of Dilithium Dibenzopentalenide



a reasonable description of such systems. Furthermore, this dianion on the basis of the above model is expected to give and experimentally does give a good correlation of nmr chemical shifts with charge density in contrast to a recent report dealing with other polycyclic dianions.³

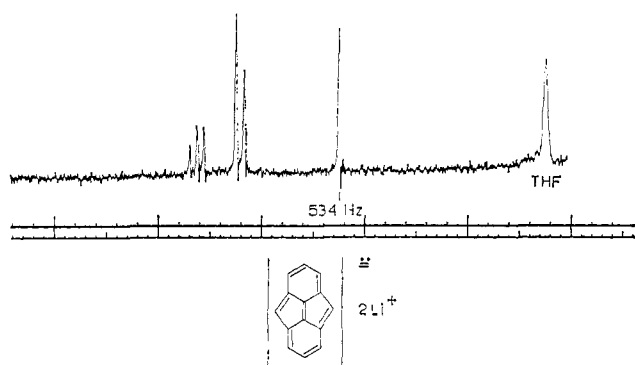


Figure 1. Nmr spectrum of dianion II.

Chart I shows those compounds on the synthetic route to the dianion II.⁴ 4,5-Methylenepheneanthrene (III) on treatment with iodic acid in aqueous acetic acid and dioxane affords a 68% yield of 4,5-methylene-9,10-phenanthraquinone (IV): mp 260° dec; ir (CHCl₃) 1680 cm⁻¹. Treatment of this material with *p*-toluenesulfonylhydrazide followed by chromatography on silica gel affords a 68% yield of 9-diazo-10-keto-4,5-methylenepheneanthrene (V): mp 180–181° dec; ir (CHCl₃) 2100, 2080, 1632, 1610 cm⁻¹. Photolysis of the diazo ketone at 3500 Å in the presence of *t*-butylamine followed by tlc affords the corresponding Wolff

(3) R. G. Lawler and V. Ristagno, *J. Amer. Chem. Soc.*, **91**, 1534 (1969). The discrepancy in the charge density–chemical shift correlation for the compounds reported can be ascribed to an incorrect ring current adjustment. In some of the molecules considered by Lawler and Ristagno, a paramagnetic ring current for the dianion would be expected—a suggestion that would account for the abnormally high shifts. For dianions possessing $(4n + 2)$ π electrons in a monocyclic array, a good correlation is anticipated: see above; T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41** 966 (1963); R. S. Schneider and E. F. Ullman, *Tetrahedron Lett.*, 3249 (1969).

(4) All new compounds showed satisfactory analytical data.

rearrangement amide VI (ir (CHCl₃) 3425, 1670 cm⁻¹) in 2% yield. The low yield in this reaction is both interesting and frustrating in view of the observed propensity for the Wolff rearrangement to occur under electron-impact conditions.^{1b} Acid hydrolysis of the amide produces a 90% yield of 4,8-dihydrodibenzopentalene-4-carboxylic acid (VII) [mp 222.0–223.5°; ir (CHCl₃) 1703 cm⁻¹; nmr τ (CDCl₃) –0.30 (1 H, bs), 2.56, 2.65, 2.83 (6 H, ABC pattern broadened by allylic methine and methylene coupling, $J_{ab} = J_{ac} = 7.6$ Hz, $J_{bc} = 1.5$ Hz), 4.43 (1 H, s), 5.69 (2 H, s)] which on copper quinoline decarboxylation affords 4,8-dihydrodibenzopentalene (VIII), mp 137.5–138.3° [nmr τ (CCl₄) 2.79, 2.97 (6 H, A₂B pattern broadened by methylene coupling, $J_{ab} = 7.6$ Hz), 5.87 (2 H, s)] in 73% yield.

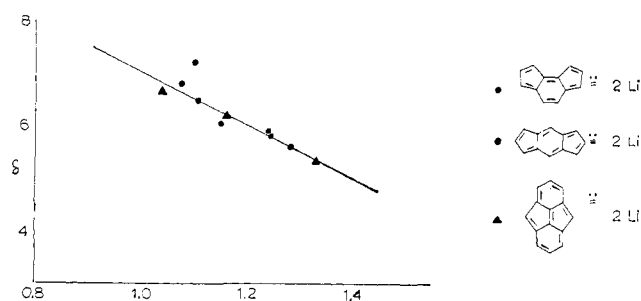


Figure 2. Plot of dianion nmr chemical shifts vs. charge density.

Treatment of dihydrodibenzopentalene (5.5 mg, 0.031 mmol) in THF-*d*₈ (0.3 ml) with *n*-butyllithium in hexane at –78° followed by warming to room temperature affords the dibenzopentalenyl dianion, whose nmr is shown in Figure 1. Inverse addition of the dianion-containing solution to D₂O produces dihydrodibenzopentalene (IX) with 99% *d*₂ incorporation (mass spectrum) in the 4 and 8 positions (nmr).

Figure 2 is a plot of the nmr chemical shift of the protons of several perturbed [12]annulene dianions⁵ vs.

(5) For the nmr spectrum of the *as*-indacene dianion see T. J. Katz, V. Balogh, and J. Schulman, *J. Amer. Chem. Soc.*, **90**, 734 (1968). We are indebted to Professor K. Hafner for providing us a copy of the nmr spectrum of *s*-indacene prior to publication.

