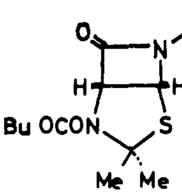
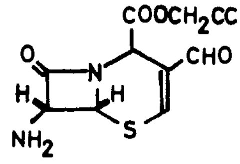


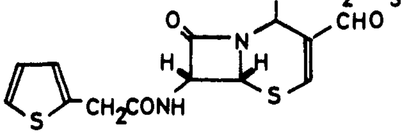
XI



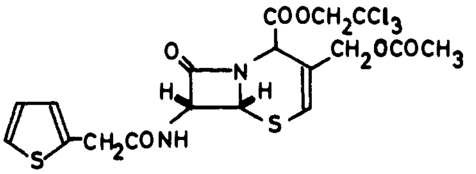
XII

XI, $[\alpha]^{20}\mathrm{D}$ $-122°$ (c 0.46, $CHCl_3$), which in trifluoroacetic acid solution at room temperature during 2.5 hr was transformed to the aminoaldehyde XII, λ_{max} 292 mμ (13,600, EtOH); this sensitive intermediate was used in subsequent reactions without extensive purification.

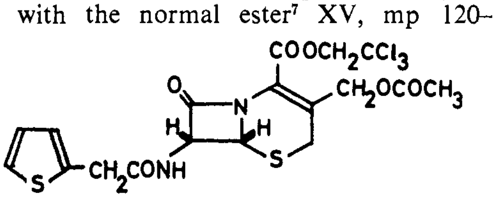
Condensation of the aminoaldehyde XII in benzene with thiophene-2-acetyl chloride in the presence of pyridine led to the amide[7] XIII, mp 135–135.5°, $[\alpha]^{20}\mathrm{D}$ $+485°$ (c 1.14, $CHCl_3$), which was treated in tetrahydrofuran solution with diborane, followed by pyridine–acetic anhydride, to give isocephalothin β,β,β-trichloroethyl ester[7] (XIV), mp 102°, $[\alpha]^{20}\mathrm{D}$ $+320°$ (c 1.01, $CHCl_3$). When the iso ester was allowed to stand in anhydrous pyridine solution at room temperature during 3 days it was smoothly equilibrated ($K_{\mathrm{normal/iso}} = {}^1/_3$) with the normal ester[7] XV, mp 120–123°, $[\alpha]^{20}\mathrm{D}$ $+14°$ (c 0.95, $CHCl_3$), which was easily separated by chromatography on silica gel, and reduced by zinc dust in 90% aqueous acetic acid at room temperature to cephalothin (II), mp 160–160.5°, $[\alpha]^{20}\mathrm{D}$ $+50°$ (c 1.03, CH_3CN), whose properties were identical in all respects with those of material prepared from natural cephalosporin C.[5]



XIII

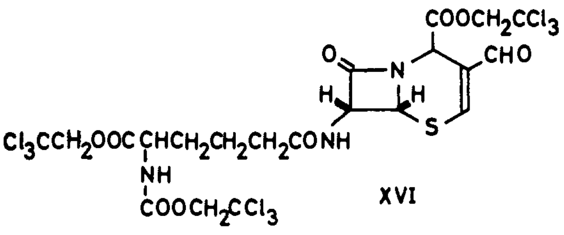


XIV

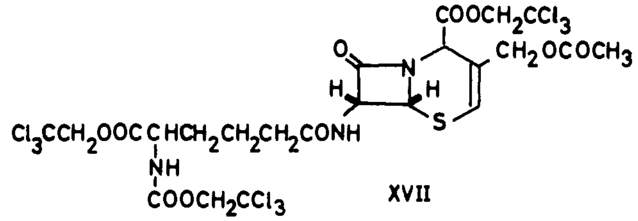


XV

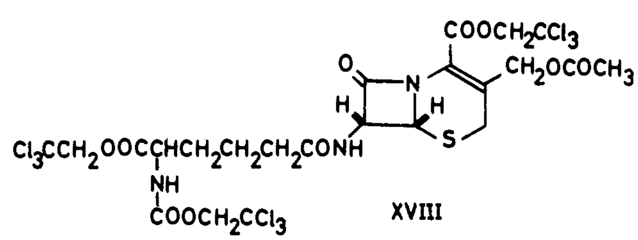
In another series of reactions the aminoaldehyde XII was condensed in tetrahydrofuran with N-β,β,β-trichloroethyloxycarbonyl-D-(−)-α-aminoadipic acid,[7] mp 137.5°, $[\alpha]^{20}\mathrm{D}$ $-8°$ (c 1.03, 1 N NaOH), in the presence of dicyclohexylcarbodiimide. The crude reaction mixture was esterified, using β,β,β-trichloroethanol in methylene chloride in the presence of dicyclohexylcarbodiimide and pyridine. Elution of the resulting material from silica gel by benzene–ethyl acetate (3:1) gave two products, of which XVI was the more polar, since it was converted by reduction in tetrahydrofuran with diborane, followed by acetylation with acetic anhydride–pyridine to the iso ester[7] XVII, mp 111–114°, $[\alpha]^{20}\mathrm{D}$ $+220°$ (c 1.01, $CHCl_3$). When the latter was allowed to stand in pyridine at room temperature for 3 days, it was equilibrated ($K_{\mathrm{normal/iso}} = {}^1/_4$) with the normal ester[7] XVIII, mp 157–159°, $[\alpha]^{20}\mathrm{D}$ $+40°$ (c 0.76, $CHCl_3$), which was easily separated by chromatography on silica gel and reduced by zinc dust and 90% aqueous acetic acid at 0° during 2.5 hr to cephalosporin C (I), identical with natural material in paper chromatographic behavior, and in antibacterial activity against *Neisseria catarrhalis*, *Alcaligenes faecalis*, *Staphylococcus aureus*, and *Bacillus subtilis*; further, the synthetic crystalline barium salt, $[\alpha]^{20}\mathrm{D}$ $+80°$ (c 0.57, H_2O), was identical in optical rotation and spectroscopic properties with the salt of natural cephalosporin C.



XVI



XVII



XVIII

Acknowledgment. We are pleased to acknowledge the very generous support we have received from CIBA, Ltd., and especially the never-failing confidence and encouragement of Dr. Albert Wettstein.

R. B. Woodward, K. Heusler
J. Gosteli, P. Naegeli, W. Oppolzer
R. Ramage, S. Ranganathan, H. Vorbrüggen
Woodward Research Institute
4000 Basel 7, Switzerland

Received January 3, 1966

Pyracyloquinone

Sir:

Although Hückel's $4n + 2$ rule strictly applies only to monocyclic hydrocarbons, polycyclic aromatics possessing this number of π electrons are frequently misnamed Hückel aromatics. Nevertheless, the simple LCAO calculations do predict these compounds to have a high resonance energy. Brown[1] predicted that pyracylene (I), a $4n + 2$ aromatic hydrocarbon, should

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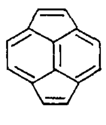
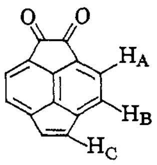
(1) R. D. Brown, *J. Chem. Soc.*, 2391 (1951).

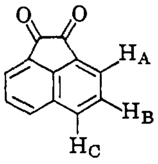
have a resonance energy of 5.4156β; Dauben[2] estimated a strain energy of about 52 kcal/mole. The unique feature of the electronic structure of this molecule is the prediction that it will have an empty nonbonding molecular orbital—the simplest hydrocarbon predicted to have this electronic configuration.[1,3] Stubbs and Tucker[4] synthesized dibenzpyracylene; Anderson[5] has failed in many attempts to synthesize the parent hydrocarbon. There have been no reports of simple naphthalene derivatives in which both *peri* positions are bridged by two sp^2 carbons. We wish to report the synthesis of such a system, the quinone (II) derived from pyracylene.



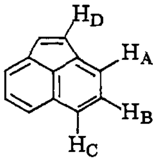
I



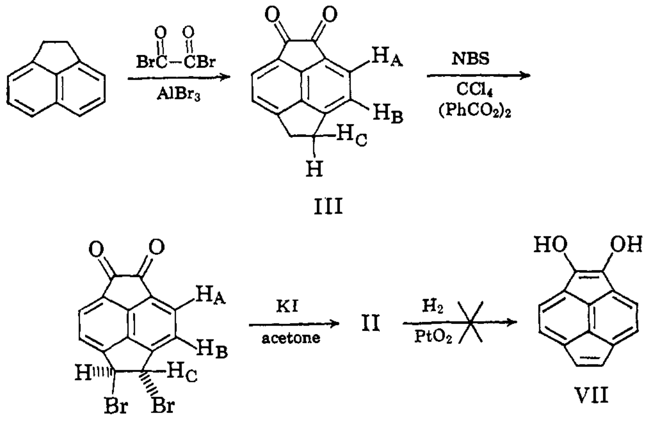
II



V



VI



1,2-Diketopyracene (III), mp 305–308°, was prepared by the method of Richter and Stocker[6,7] [$\nu_{\max}^{\mathrm{KBr}}$ (cm^{-1}) 3050, 2925, 1735, and 1660; $\lambda_{\max}^{\mathrm{C_2H_5OH}}$ (mμ (ϵ)) 213 (43,000), 238 (52,500), 246 (48,200), 318 (sh, 4950), 332 (6400), 354 (6700), and 364 (sh, 5600)]. Its nmr spectrum (see Table I) supports the symmetrical substitution of the naphthalene ring. N-Bromosuccinimide converted III into 1,2-diketo-5,6-dibromopyracene,[8] yellow flakes, mp 189–191° dec, in approximately 60% yield [$\nu_{\max}^{\mathrm{CHCl_3}}$ (cm^{-1}) 1740 and 1660; $\lambda_{\max}^{\mathrm{C_2H_5OH}}$ (mμ (ϵ)) 225 (33,200), 231 (34,200), 243 (sh, 18,600), 324 (7700), and 332 (7800)]. Dehalogenation proceeded in 90–95% yield utilizing powdered potassium iodide in refluxing acetone. The product,[8] orange flakes, did not melt up to 350° although some decomposition was noted at about 300°. Its spectral data fully support structure II, for which we propose the name pyracyloquinone [$\nu_{\max}^{\mathrm{CHCl_3}}$ (cm^{-1}) 1735 and 1685; $\lambda_{\max}^{\mathrm{C_2H_5OH}}$ (mμ (ϵ)) 230 (28,500), 245 (17,900), 307 (17,500), 314 (17,000), and 346 (7120)]. Its nmr spectrum (see Table I) showed a considerable deshielding[9] of both H_B and H_C relative to the comparable protons in compounds III, V, and VI. This observation indicates an appreciable ring current effect in pyracyloquinone.

Table I. Nmr Spectra[a] of Acenaphthalene Derivatives

Compd	H_A	H_B	H_C	H_D	$J_{A,B}$	$J_{B,C}$	$J_{A,C}$
II[b,e]	8.26	8.26	7.69				
III[c,f]	8.12	7.72	3.76		8.0		
IV[c,g]	8.25	7.91	6.09		7.5		
V[d,f]	7.95	7.12	7.75		7.5	7.0	1.0
VI[d,e]	7.90	7.58	7.79	7.15	7.5	7.5	1.0

[a] Chemical shifts are in parts per million relative to TMS as an internal standard. [b] The naphthalene ring protons collapsed to an A_2 system. [c] AB spectrum. [d] ABC spectrum. [e] DMSO-d_6 solvent. [f] CF_3CO_2H solvent. [g] $CDCl_3$ solvent.

Further confirmation of the structure was provided by its catalytic hydrogenation. Compound II almost instantaneously absorbs 1 mole of hydrogen to produce III in quantitative yield. The reactivity of the double bond accentuates the high degree of strain involved in bridging naphthalene with two sp^2 carbons in both *peri* positions. The lack of any reduction of the quinoid grouping[10] suggests that the delocalization energy of the pyracylene system may not be sufficient to overcome the large amount of strain energy—contrary to predictions based on molecular orbital theory.

Acknowledgment. We wish to thank the Petroleum Research Foundation (Grant No. 539-G1) and the Wisconsin Alumni Research Foundation for partial support of this work.

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(2) H. J. Dauben, Abstracts, 130th National Meeting of the American Chemical Society, New York, N. Y., 1956, p 37D.

(3) (a) B. M. Trost, unpublished calculations; (b) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π Electron Calculations," W. H. Freeman and Co., San Francisco, Calif., 1965.

(4) H. W. D. Stubbs and S. H. Tucker, *J. Chem. Soc.*, 2936 (1951).

(5) A. G. Anderson, Jr., and R. G. Anderson, *J. Org. Chem.*, **23**, 517 (1958), and references therein.

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

(7) Although these workers confirmed the structure of III by chemical degradation, they reported no spectral properties. These data, presented here, fully confirm this assignment. The shift to higher frequency of the carbonyl absorption in the infrared spectrum of III compared to V ($\nu_{\max}^{\mathrm{KBr}}$ 1720 cm^{-1}) exemplifies the increased strain. When naphthalene is bridged by two carbons in the 1,8 positions, the aromatic ring shortens this distance by increasing the distance between the opposite *peri* positions. This method to release strain is no longer available in III.

(8) Satisfactory elemental analyses were obtained for all new compounds.

(9) The deshielding of these protons relative to the model compounds becomes more striking when corrections for solvent differences are applied.

(10) Treatment of II with other reducing agents such as zinc, sodium, and triethyl phosphite, which should attack at the quinoid system, will be reported in a future communication.

Barry M. Trost
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received November 29, 1965

Unusual Metalloporphyrins. I. Preparation of Chromium Mesoporphyrin IX Dimethyl Ester[1]

Sir:

To our knowledge a chromium porphyrin has never been prepared by the application of any of the standard synthetic methods.[2] Recently, Elvidge and Lever[3] isolated a chromium phthalocyanine complex which has a structure similar to a metalloporphyrin. This indicates that the preparation of chromium porphyrin was feasible if a fresh synthetic approach could be found.

(1) Elemental Organic Compounds. XVII.

(2) J. F. Taylor, *J. Biol. Chem.*, **135**, 569 (1940).

(3) J. A. Elvidge and A. B. P. Lever, *J. Chem. Soc.*, 1257 (1961).