Tetrahedron Letters, Vol.29, No.9, pp 983-986, 1988
Printed in Great Britain

0040-4039/88 $3.00 + .00
Pergamon Press plc

THE SYNTHESIS AND NOVEL STRUCTURE OF METHYL 7-PHENYL-DIBENZ[*a,j*] ANTHRACENE-14-CARBOXYLATE AND METHYL 5-PHENYL-BENZO[1,2-*h*:5,4-*h'*]DIQUINOLINE-3-CARBOXYLATE: RIGID SEMI-HELICAL AROMATIC SPACERS WITH CONVERGENT FUNCTIONAL GROUPS

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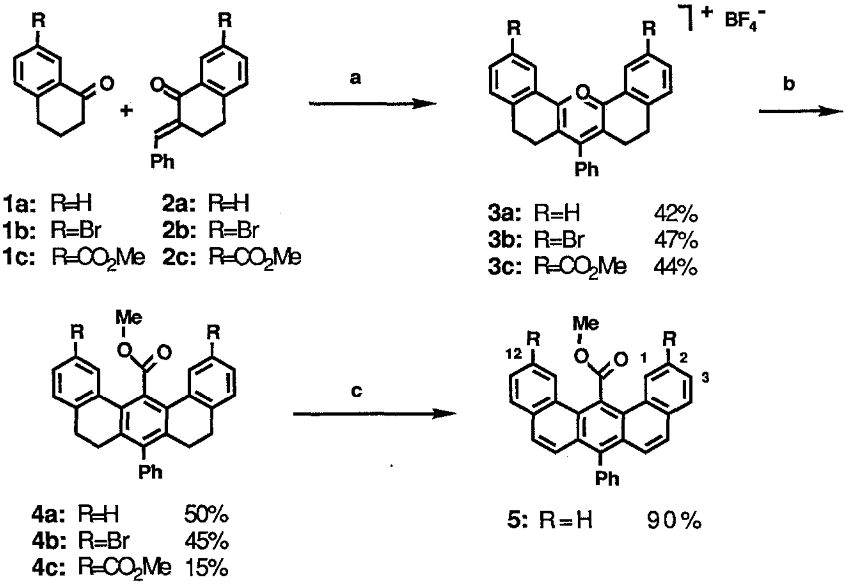
Abstract: The synthesis and structure of two novel polycyclic aromatic systems is presented. These systems can act as rigid spacer units for the construction of receptors and synthetic reagents possessing different degrees of helicity and containing convergent functional groups.

Rigid molecular spacer units have widespread utility in bioorganic chemistry as a result of their ability to hold groups with well defined separations and orientations. Indeed, bi- and tricyclic aromatic systems have been used to link porphyrins[1a] and crown ethers[1b] and to create molecular clefts of varying dimensions.[1c] Other rigid spacers include Whitlock's diyne unit,[2] bibicyclo[2,2,2]octane,[3] and analogues of Tröger's base.[4] Additionally, very long mixed-bicyclic spacers have been used to control polymerization reactions by holding initiating and terminating groups at fixed distances.[5]

We recently described the synthesis and complexation chemistry of a "molecular tweezer" in which a dibenz[*c,h*]acridine spacer enforced a syn cofacial orientation of two acridine chromophores while it maintained an interchromophore distance of ca. 7 Å.[6] Although this spacer contains a weakly basic nitrogen atom directed into the cavity of the molecular tweezer, we were intrigued by the realization that a functional group (e.g. -CO_2H) in this position would be able to engage in better defined hydrogen bonding interactions.[7] In this Letter the synthesis of the dibenz[*a,j*]-anthracene and benzo[1,2-*h*:5,4-*h'*] diquinoline ring system is described in which an ester group is attached to the central, bay region carbon. To our knowledge the latter ring system has not previously been described. X-ray crystallographic analysis of both systems reveals their unique structure and potential for the construction of new receptors and synthetic reagents.

Ample literature precedent can be found for the conversion of simple pyrylium salts to substituted aromatic compounds but not in sterically congested systems such as **3**.[8] In the event, dibenzoxanthylium tetrafluoroborate **3a**[9] underwent smooth reaction with trimethyl phosphonoacetate and 2 equivalents of sodium hydride in THF (room temp to reflux, 2 h) to produce ester **4a** in 50% yield (Scheme 1).[10,11] The



1a: R=H **2a**: R=H
1b: R=Br **2b**: R=Br
1c: R=CO_2Me **2c**: R=CO_2Me

3a: R=H 42%
3b: R=Br 47%
3c: R=CO_2Me 44%

4a: R=H 50%
4b: R=Br 45%
4c: R=CO_2Me 15%

5: R=H 90%

a: BF_3OEt_2; **b**: $(MeO)_2POCH_2CO_2Me$, 2 equiv. NaH, THF; **c**: DDQ, PhCl, Rflx

Scheme 1

generality of this conversion is demonstrated by the synthesis of substituted spacers **4b** and **4c**. The functionality at C(2) and C(12) is important for elaboration into clefts and cavities into which the functional group will be oriented.

Ester **4a** was dehydrogenated with DDQ in refluxing chlorobenzene to produce dibenzanthracene **5** in 90% yield. Its structure was determined by X-ray crystallography and found to be highly distorted (Figure 1).[12] In order to relieve unfavorable nonbonded interactions between the ester group and H(1) and H(13), the molecule has adopted a marked helical twist in which C(2) and C(12) deviate from the mean plane of the dibenzanthracene system by -0.68 Å and 0.75 Å, respectively.[13] The aromatic system is twisted 43° from end to end. Strikingly, the C(2) to C(12) distance which is 7.24 Å in dibenz[*c,h*]acridine[14] is 8.20 Å in **5** as a result of (1) the twist, (2) increased C(13a)-C(14) and C(16)-C(16a) bond lengths (ca. 1.47 Å), and (3) decreased C(5)-C(6) and C(8)-C(9) bond lengths (ca. 1.33 Å).

In order to produce a spacer with a C(2)-C(12) distance closer to that required for a molecular tweezer (ca. 7 Å),[6] benzodiquinoline **10** was synthesized as outlined in Scheme 2. Suprisingly, the coupling of quinolone **6** and its benzylidene **7** produced pyran **8** (54% yield) which did not oxidize under the reaction conditions. The pyrylium

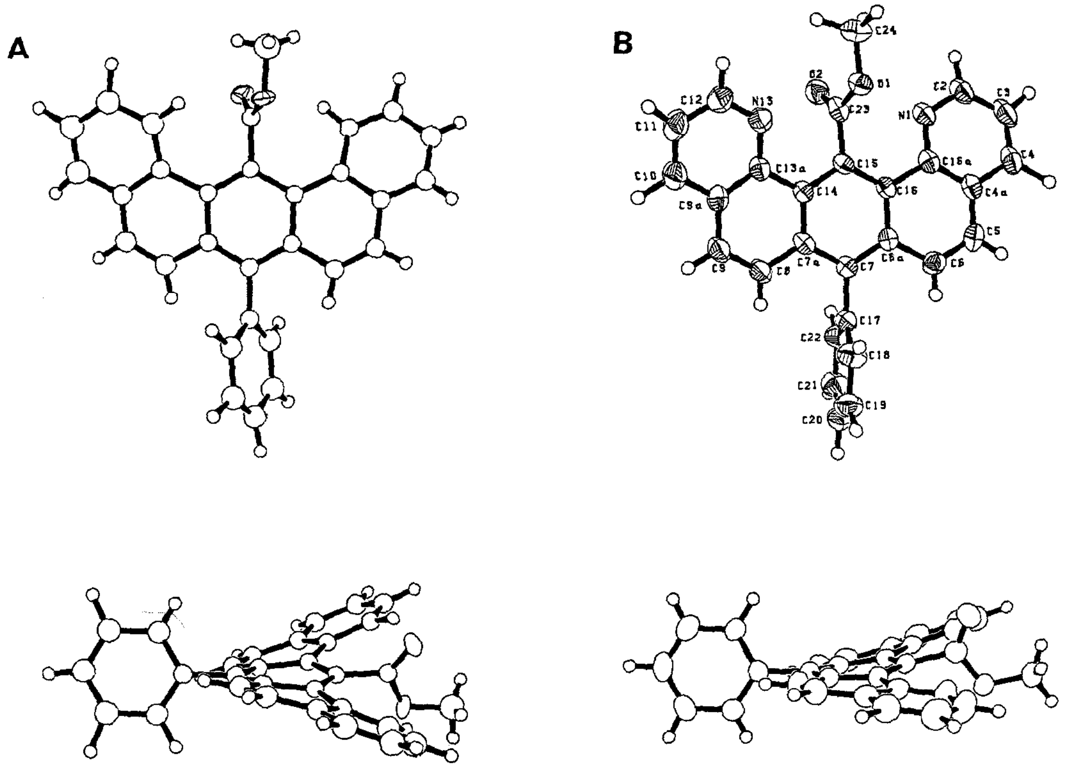
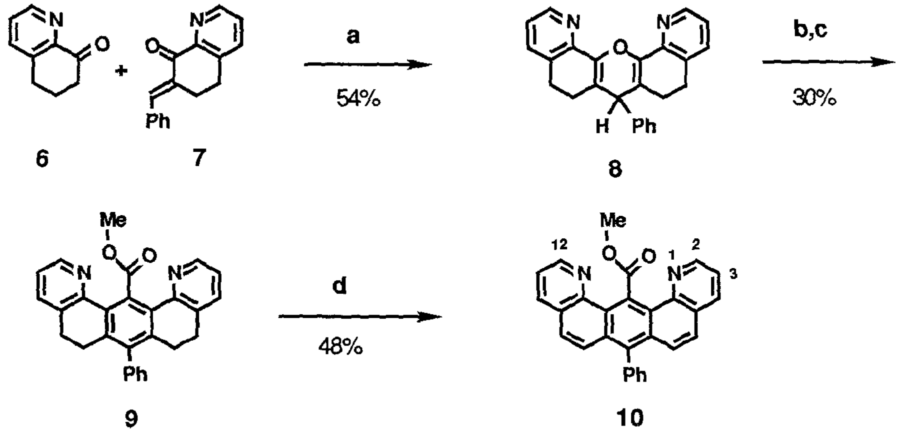


Figure 1: Two ORTEP drawings of (A) ester **5** and (B) ester **10**. Thermal ellipsoids represent 35% probability contours. The dibenz[*a,j*]anthracene numbering system is used.



a: BF_3OEt_2; b: DDQ, CH_2Cl_2; c: $(MeO)_2POCH_2CO_2Me$, 2 equiv. NaH, THF; d: DDQ, PhCl, Rflx

Scheme 2

salt could be obtained by treatment with DDQ (CH_2Cl_2, room temp). Subsequent condensation with trimethyl phosphonoacetate (THF, NaH, room temp) produced ester **9** in 28% yield and dehydrogenation with DDQ (PhCl, reflux) afforded the fully aromatic spacer **10** (48% yield) which was analyzed by X-ray crystallography.

As expected, the structure of **10** is much less distorted (Figure 1). The C(2)-C(12) distance is 7.52 Å and the twist is 27° from end to end. As in ester **5**, C(2) and C(12) deviate from the mean plane of the aromatic system, in this case by -0.42 Å and 0.46 Å, respectively. Although both N(1) and N(13) have close contacts with the C(23) of the ester (ca. 2.60 Å) it is planar and has normal bond lengths and normal spectroscopic properties (IR: 1719 cm^{-1}; ^{13}C NMR 174.7 ppm).

In conclusion, two new classes of rigid spacer units have been developed. These compounds are easily synthesized and have unique structural features which include helicity and convergent functionality. The construction of new receptors and catalytic systems incorporating these units is in progress in these laboratories.

Acknowledgement: The author thanks Scott Wilson for assistance with the X-ray analyses. Funding from the American Cancer Society (Junior Faculty Award) and the National Institutes of Health (GM38010-01) is gratefully acknowledged.

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12. Full details of the X-ray analyses will be published in due course.
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(Received in USA 24 November 1987)