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Note

Crystal structure of and conformational equilibria in 1, 1′-dihydroxybis(4*H*-cyclopenta[*def*]phenanthrene) and related derivatives

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The aromatic protons and carbons in the NMR spectra of certain clamped 1,1,2,2-tetraarylethane-1,2-diols undergo intermediate exchange at ambient temperature as the result of conformational equilibrium between two enantiomeric *gauche* forms. The crystal structures for two of these derivatives show the conformational preference for this geometry in the solid state in contrast to other reported unclamped 1,1,2,2-tetraarylethane-1,2-diols. The conformational preference of these vicinal diols parallels that for the 1,1,2,2-tetraarylethanes. However, in the asymmetrically substituted diphenylmethylfluorene series, the vicinal diol prefers to adopt a *gauche* conformation in contrast to the hydrocarbon which prefers the *anti* geometry attributed to hydrogen bonding effects in the former. The results of AM1 calculations for the conformational preferences of this series of diols and ethanes are included and agree with experimental observations. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ethane-1,2-diols; conformation; hydrogen bonding

INTRODUCTION

Steric crowding in ethanes can result in an increase in the rotational barrier and the exhibition of stable diastereomeric and enantiomeric rotamers. Examples of this class of compounds include the triptycenes which are substituted with a bulky tertiary or secondary carbon at the bridgehead position,[1,2] and other tetrasubstituted ethanes carrying bulky substituents.[3,4] Electronic effects such as intramolecular hydrogen bonding in vicinal diols can further restrict rotation about carbon–carbon σ-bonds, although such interactions are not as energetically strong as hydrogen bonding in 1,3-diols where the more ideal six-centered arrangement can be achieved.[5] Nevertheless vicinal diols contain the highest proportion of intramolecular H-bonded conformers.[6] This has been explained in terms of the magnitude of the entropy factor.[7] According to Buckley and Giguere,[8] ethanediol is present in the *gauche* form only in the gas phase as well as in dilute solution. In our investigations of the photochemistry of some 1,1,2,2-tetraarylethane-1,2-diols, we observed some unusual exchange phenomena in the NMR spectra of 1, 1′-dihydroxybis(4*H*-cyclopenta[*def*]phenanthrene) (**1**) and 1, 1′-dihydroxybis(9*H*-fluorene) (**2**). We also report on the crystal structure of **1**, which concurs with the solution data for its conformation.

RESULTS AND DISCUSSION

Diols **1** and **2**[9] were prepared by reductive coupling, in the presence of zinc, of 4*H*-cyclopenta[*def*]phenanthrene-4-one and fluorenone, respectively, according to the procedures described by Tanaka *et al.*[9] The room temperature ^{1}H NMR spectrum of **1** showed a signal at δ 7.30 ppm and a broad peak at 7.62 ppm for all 16 aromatic protons [Fig. 1(a)]. Upon cooling to −40 °C, eight distinct aromatic signals could be observed with the expected multiplicity associated with a C_2 symmetry [Fig. 1(b)]. The ^{13}C NMR spectrum of diol **1** showed a similar temperature dependence where seven aromatic carbon signals (the aliphatic carbon signal appears at δ 89.7 ppm) are observed under ambient conditions but on cooling to −40 °C these were resolved into 14 signals.

What is interesting is the large changes in chemical shifts of the aromatic protons and carbon signals at the extreme temperatures. The aromatic proton signals range from δ 5.9 to 8.3 ppm in the low-temperature spectrum, suggesting a conformation involving very deshielded and shielded hydrogen nuclei consistent with a *gauche* geometry expected from intramolecular hydrogen bonding of a vicinal

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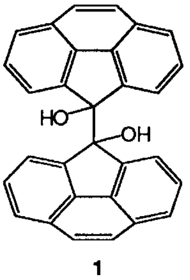

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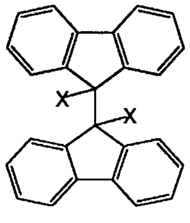

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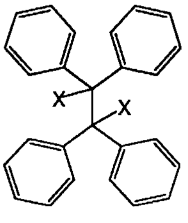

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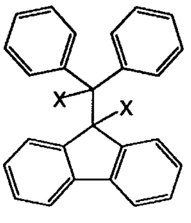

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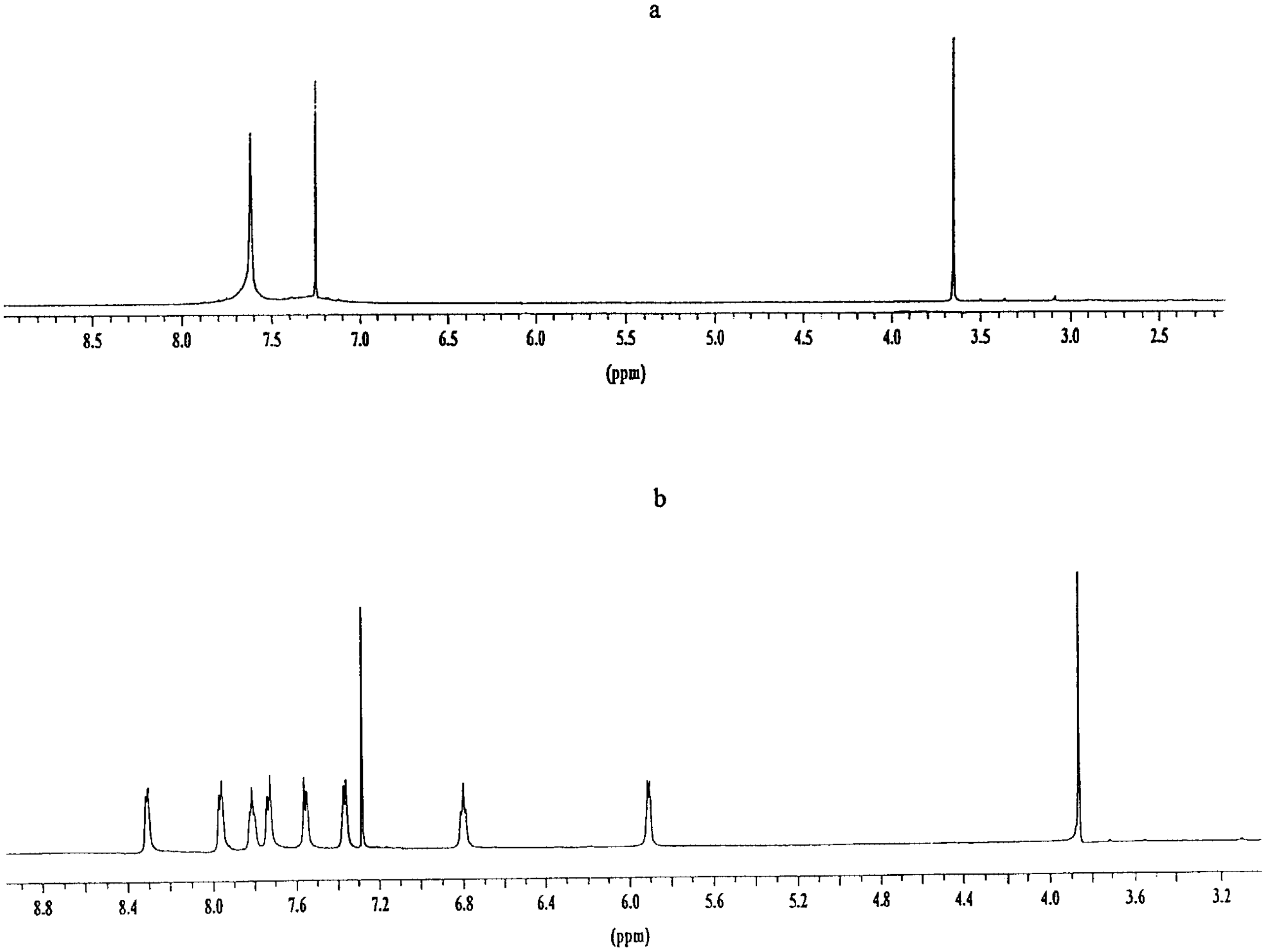
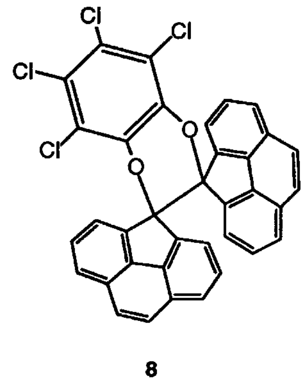


Figure 1. ^{1}H NMR spectra (600 MHz) of diol **1** at (a) 25 and (b) −40 °C.

diol. Such a geometry would place one of the *peri*-hydrogens directly in the shielding cone of the other aromatic moiety.



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The x-ray crystal structure of diol **1** was determined and shows very clearly the C_2 *gauche* conformation and the proximity of one of the *peri*-hydrogens to the other aromatic ring (Fig. 2). The low-temperature ^{1}H NMR spectrum of **1** is remarkably similar to that of a Diels–Alder adduct **8**[10] (Fig. 3) in which bond rotation about the C—C bond between the two aromatic moieties is completely restricted. Since such intramolecular hydrogen bonding forces are relatively weak for 1,2-diols, increasing the temperature should overcome the rotational barrier and give a ^{1}H NMR spectrum for **1** averaging C_{2v} geometry. A higher boiling solvent (DMSO) was used for the high-temperature NMR spectra. The room temperature ^{1}H NMR spectrum of **1** in this solvent is similar to that in $CDCl_3$. The high-temperature spectrum of **1** at 82 °C gave three signals in the aromatic region (δ 7.0–7.8 ppm) with relative intensities of 4 : 2 : 2. In addition, the OH signal

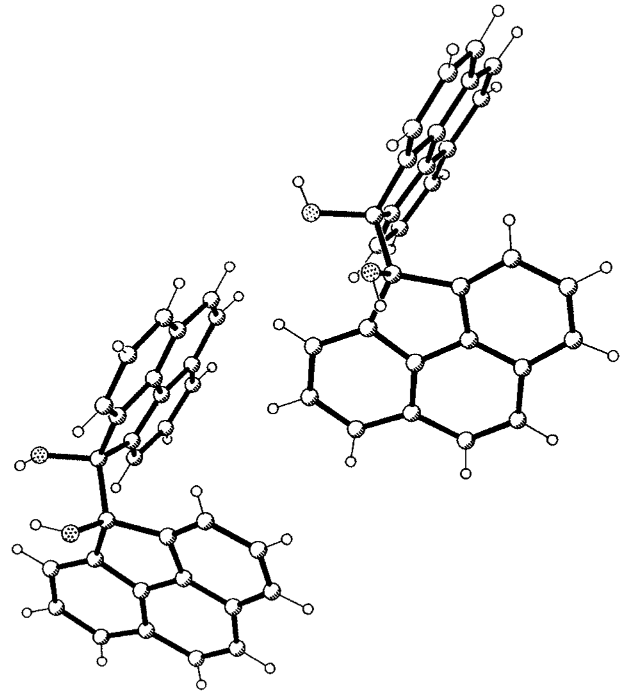

Figure 2. X-ray crystal structure of diol **1**. Element key: carbon, partially hatched circles; oxygen, dotted circles; hydrogen, small open circles.

appearing at δ 6.3 ppm at room temperature broadens and shifts to higher field (δ 5.5 ppm) at 82 °C. The C_{2v} averaged structure for **1** would exhibit four distinct aromatic signals. It is possible that two of the signals overlap under these conditions, as is evident from the relative intensities of the three observed signals.

Similar behavior was seen in the ^{1}H NMR spectrum for diol **2**. The low-temperature (−63 °C) spectrum of **2** in CD_2Cl_2 showed eight signals in the aromatic region with partial overlap between two of these. A very shielded signal was observed at δ 5.80 ppm which we attribute to the pair of *peri* aromatic hydrogens in proximity to the shielding cone of the other fluorene moiety, in a similar fashion to diol **1**. Pascal *et al.*[11] reported broad signals for **2** at 20 °C which become resolved into four signals at 60 °C. They interpreted this behavior to conformational equilibria between the *anti* and *gauche* forms of this diol (Fig. 4). Such an equilibrium would not give the low-temperature spectrum which we observe for diol **2**. The *anti* conformation of this diol would have C_{2v} symmetry and show four aromatic proton signals. With the expected eight aromatic proton signals of the *gauche* conformer, the low-temperature ^{1}H NMR spectrum for the proposed *anti–gauche* equilibrium for **2** would be expected to be much more complex.

Unlike diols **1** and **2**, the crystal structure of 1,1,2,2-tetraphenylethane-1,2-diol (**3**) is exclusively in the *anti* conformation.[12] This contrasting behavior between diols **1** and **2** and diol **3** in their conformational preferences is similar to that between 9,9′-bifluorenyl (**5**) and 1,1,2,2-tetraphenylethane (**6**) in which the former exists as the *gauche* conformer and the latter as the *anti* conformer.[13] The explanation provided for the contrasting conformational preference in the hydrocarbons is the ability for the geminal phenyl substituents in **6** to adopt a twisted geometry enabling these to stack or nest by π-interaction which would diminish geminal repulsion and result in a decrease in the valence angle. Such a decrease in the valence angle would minimize vicinal interactions, which leads to an *anti* preference for conventional reasons. By contrast, the planar fluorene substituents in **5** would favor the *gauche* conformer because of the proximity of the *peri*-hydrogens (H-1 and H-8) between the two fluorene groups in the *anti* conformer leading to a destabilization of 6.6 kcal mol^{-1} (1 kcal = 4.184 kJ) relative to the *gauche* form.

We performed semi-empirical (AM1) calculations for diols **1–4** in order to establish the importance of intramolecular hydrogen bonding in determining conformational preference in these systems. The energy differences between the *gauche* and *anti* conformers were determined and compared with the values for the corresponding tetrasubstituted ethanes. The results indicate that the conformational preference for both the diols and the hydrocarbons correlate (see Table 1). For the bisfluorene series, the *gauche* form is preferred by 4.4 and 5.2 kcal mol^{-1} for the diol **2** and hydrocarbon **5**, respectively. On the other hand, the *anti* conformation is preferred in the tetraphenyl-substituted series **3** and **6**. For the asymmetric series **4** and **7**, the *gauche* form is slightly preferred over the *anti* form in the diol but the reverse preference is observed for the hydrocarbon **7**. The room temperature ^{1}H NMR spectrum of diol **4** shows a complex pattern of signals associated with the fluorene ring intermediate between a C_{2v} and C_2 structure. Such a spectrum may be rationalized in terms of an intermediate exchange between the two enantiomeric *gauche* conformers. The low-temperature ^{1}H NMR spectrum (−60 °C) of **4** shows a more complicated spectrum which is probably associated with the freezing out of and resultant asymmetry of the twisted phenyl groups. The crystal structure of **4** clearly shows the *gauche* conformation (Fig. 5). It must be noted, however, that crystal structures do not necessarily correlate with those in solution. The contrasting behavior between **4** and **7** as determined by semi-empirical calculations may be ascribed to intramolecular hydrogen bonding effects in the case of **4**, although the same effects should increase the conformational preference in the case of diols **2** and **3** relative to the corresponding hydrocarbons **5** and **6**, respectively. The calculated conformational energies for this series point to a greater preference towards the *anti* form in the diols, indicating that intramolecular hydrogen bonding may not be a significant factor in determining conformations in these derivatives. Electronic and steric effects associated with the aryl substituents may be the predominant factors in establishing their geometry.

Supporting information available

^{13}C NMR spectra for diol **1** at ambient temperature and −40 °C and the ^{1}H spectra in DMSO-d_6 at 80 °C are available. Variable-temperature proton spectra for diol **2** are also included. The x-ray crystallographic data including geometric coordinates for diol **1** are available. A summary of selected crystallographic data for diol **4** is also included.

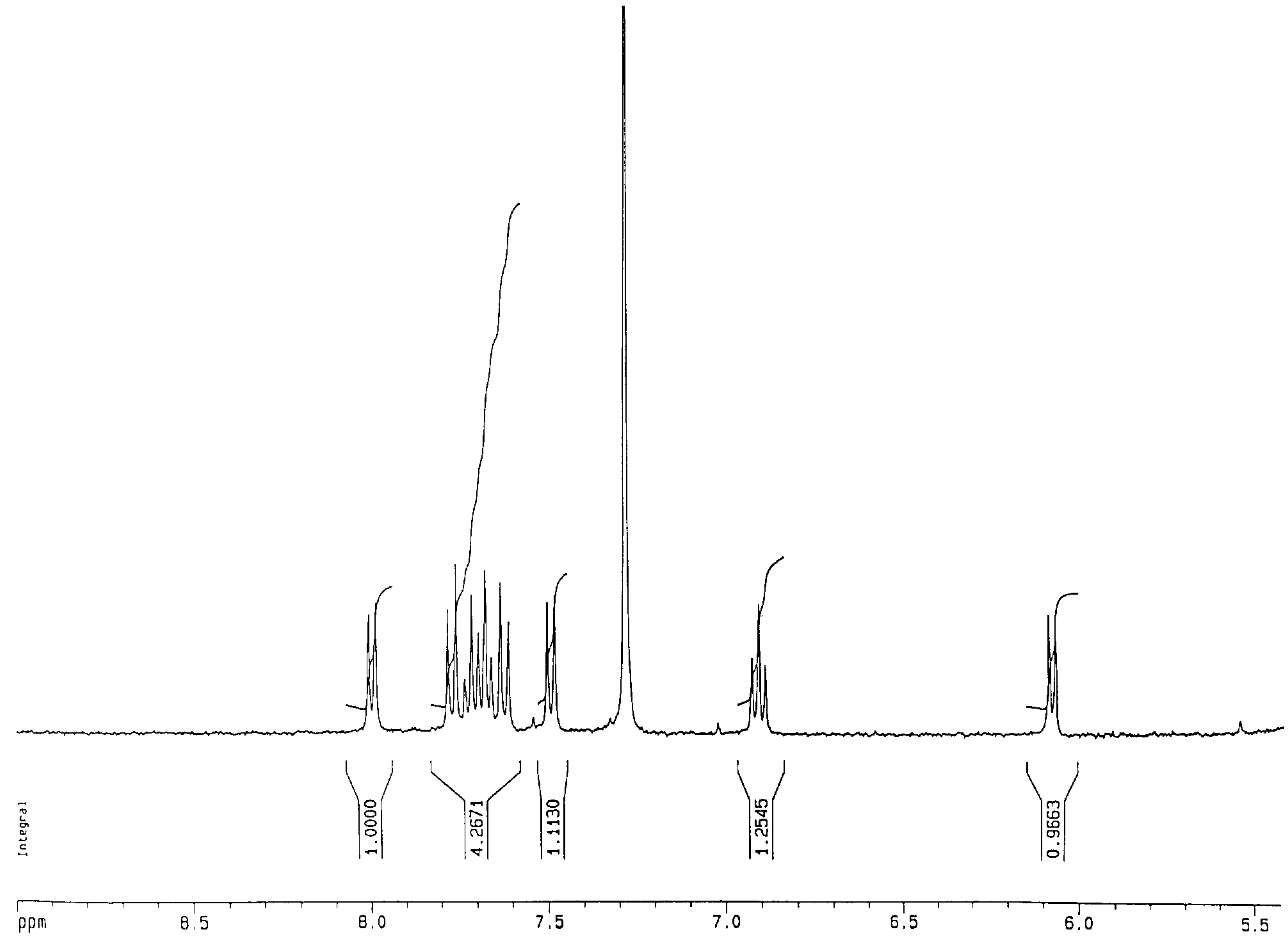

Figure 3. ^1H NMR spectrum (400 MHz) of Diels–Alder adduct **8**.

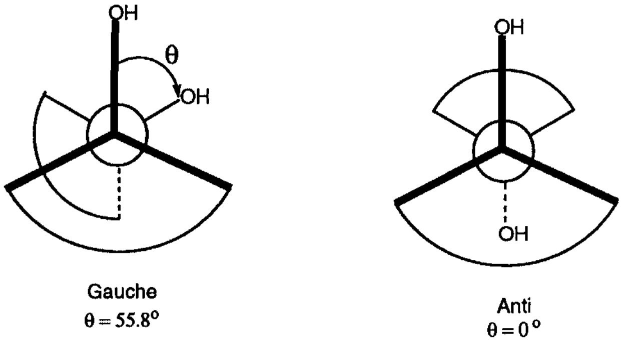

Figure 4. Conformations of diols **1** and **2**.

Table 1. Conformational energies of 1,1,2,2-tetraaryldiols and-ethanes

Compound	$E_{gauche} - E_{anti}$ (kcal mol^{-1})	Calculated dihedral angle, θ(°)[a]	Experimental dihedral angle, θ(°)
Diol **1**	−3.4	63.7	55.8
Diol **2**	−4.4	64.1	—
Diol **3**	+9.6	180.0	—
Diol **4**	−1.4	46.6	47.1
Ethane **5**	−5.2(−6.6)[b]	73.7 (65.8)[b]	59.7[c]
Ethane **6**	+5.8(+5.0)[b]	179.1	—
Ethane **7**	+1.3(+0.6)[b]	179.1	—

[a] Dihedral angle for the low-energy conformer.
[b] Calculated from EFF molecular mechanics.[13]
[c] Ref.[13].

EXPERIMENTAL

Spectra

All solvents were purified and dried by standard procedures. Infrared (IR) spectra were recorded on an HP-2000 FTIR spectrometer in KBr pellet form. ^1H and ^{13}C NMR spectra were obtained on Bruker ARX-400 and AVANCE-600 NMR spectrometers using $CDCl_3$ and DMSO-d_6 as solvent, respectively. These spectra were obtained using the zg30 pulse program with processing on a Silicon Graphics O2 workstation using the Bruker XWIN-NMR software. Mass spectra were measured on a VG Micromass 16F instrument at 28 eV or a Kratos Profile spectrometer.

Compounds

Diol **2** was prepared by a modified literature method[14] involving reductive coupling of fluorenone as described below for the preparation of diol **1**. Diol **4** was prepared by a literature procedure[15] involving phenylation of methyl 9-hydroxy-9-fluorene carboxylate.

Diol 4

M.p. 138–140 °C (lit.[15] m.p. 138–160 °C, depending on the solvent used for crystallization. ^1H NMR: δ 7.49 (d, 6H), 7.25

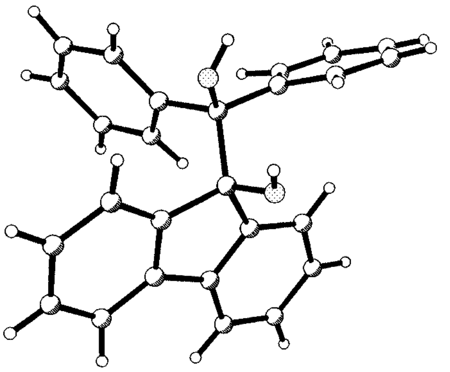

Figure 5. Crystal structure of diol **4**. Element key: carbon, partially hatched circles; oxygen, dotted circles; hydrogen, small open circles.

(t, 2H), 7.18 (m, 6H), 7.01 (t, 2H), 6.93 (d, 2H), 3.46 (br.s, 1H, OH), 3.10 (br.s, 1H, OH). ^{13}C NMR: δ 146.6, 143.0, 141.0, 129.2, 127.8, 127.5, 127.4, 127.3, 126.0, 119.6, 87.6, 81.8.

1,1′-Dihydroxybis(4H-cyclopenta[def]phenanthrene) (**1**)

A mixture of 4*H*-cyclopentaphenanthren-4-one[16] (1 g, 1.03 mmol), 1 g (15.3 mmol) of Zn powder and 0.4 g (2.9 mmol) of zinc chloride in 10 ml of 10% aqueous THF was stirred at room temperature for 4 h. The reaction mixture was worked up with 1.5 ml of 3 M HCl and the Zn was filtered off. The organic layer was taken up in toluene, washed with 3 × 5 ml of water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure. Diol **1** was isolated and obtained pure by preparative TLC (20% ethyl acetate −80% hexane) in 43% yield (0.092 g). Some 4*H*-cyclopenta[*def*]phenanthren-4-ol[16] was also obtained from this reaction in 17% yield (0.037 g) as a side product. M.p. 235–237 °C. ^{1}H NMR: δ [CDCl$_3$, room temperature; see Fig. 1(a)] 7.62–7.30 (br. s, 16 H, aromatic H), δ [CDCl$_3$, −40 °C; see Fig. 1(b)] 8.31 (d, 1H), 7.96 (d, 1H), 7.81 (t, 1H), 7.73 (d, 1H), 7.55 (d, 1H), 7.37 (d, 1H), 6.80 (t, 1H), 5.91 (d, 1H). ^{13}C NMR: δ (CDCl$_3$, room temperature) 136.5, 127.6, 127.4, 125.1, 125.3, 122.0 (br. peak), δ(CDCl$_3$, −40 °C) 144.7, 141.7, 136.2, 135.9, 127.9, 127.2, 127.1, 126.7, 125.5, 125.0, 124.96, 124.8, 123.0, 120.5. IR (KBr): 3502 cm^{-1} (OH). MS: m/z 410 (M$^+$), 392, 205, 189. Anal. Calculated for $C_{30}H_{18}O_2$: C, 87.8; H, 4.39. Found: C, 87.5: H, 4.4%.

Crystal structure determination for 1,1′-dihydroxybis(4*H*-cyclopenta[*def*]phenanthrene) (1)

Crystals of diol **1** were grown by slow evaporation from a 1 : 1 solution of CHCl$_3$ and hexane. X-ray diffraction data were collected on a Siemens SMART CCD system at the University of Windsor. A structural solution for the diol was refined in crystal system $P2_1/n$ using 5391 out of 26 237 observed reflections. The structure was solved by Direct Methods followed by Fourier Synthesis, using the SHELX 93 PC package. Final refinement was done using full-matrix least-squared procedures with anisotropic thermal parameters on all non-hydrogen atoms. The hydrogen atoms were located from the difference map and refined isotropically using a riding model (C—H 0.96 Å, $U_{11} = 0.08$ Å^2) (see Supporting information section). The final structural refinement gave cell dimensions 18.919(4) Å, 9.266(2) Å, 24.768(5), $\alpha = 90°$, $\beta = 107.03(3)°$, $\gamma = 90°$, $V = 4152(2)$ Å^3, $Z = 8$, λ(Mo Kα) = 0.71069 Å, $F(000) = 1712$, $R = 0.0568$ with data: restraints: parameter ratio of 5391 : 0 : 557. Two independent molecules are present within the unit cell.

Crystal structure determination for diol 4

Crystals of diol **4** were obtained by slow evaporation from a hexane–diethylether–methanol solution. Data were collected on a Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A combination of 1° phi and omega (with kappa offsets) scans were used.[17] The structures were solved and refined using the SHELXTL\ PC V5.1[18] package. Refinement was by full-matrix least-squares on F^2 using all data (negative intensities included). Hydrogen atoms were included in calculated positions.

Acknowledgement

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