Carbonyl and thiocarbonyl stabilized 1,4-dihydropyrazines: synthesis and characterization

David J. R. Brook, Bruce C. Noll and Tad H. Koch *

Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215, USA

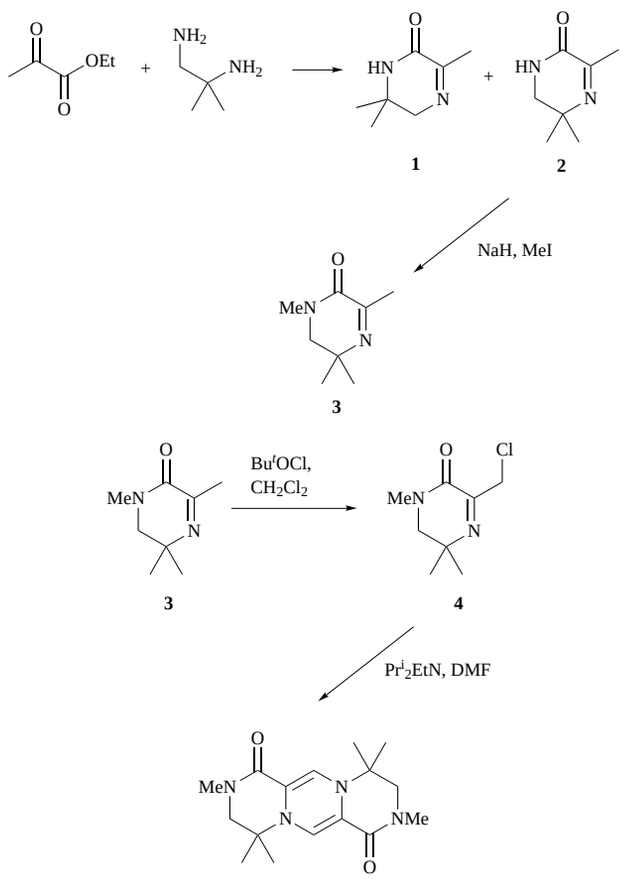
Three analogues of the 1,4-dihydropyrazine, 3,4,7,8-tetrahydro-4,4,8,8-tetramethyl-2,6-dioxa-4a,8a-diazaanthracene-1,5-dione (DDTTA), have been synthesized. 2,4,4,6,8,8-Hexamethyl-3,4,7,8-tetrahydro-2,4a,6,8a-tetraazaanthracene-1(2*H*),5(6*H*)-dione (HTTA) is synthesized by chlorination of the previously reported 5,6-dihydro-1,3,5,5-tetramethylpyrazin-2(1*H*)-one with *tert*-butyl hypochlorite and self condensation of the resulting α-chloromethylimine in the presence of diisopropylethylamine in dimethylformamide (DMF). Thioxo derivatives 3,4,7,8-tetrahydro-4,4,8,8-tetramethyl-5-thioxo-2,6-dioxa-4a,8a-diazaanthracen-1-one (DDTTA–S) and 3,4,7,8-tetrahydro-4,4,8,8-tetramethyl-2,6-dioxa-4a,8a-diazaanthracene-1,5-dithione (DDTTA–S_2) have been synthesized by direct thionation of DDTTA with phosphorus pentasulfide in pyridine. All three molecules have been characterized spectroscopically. In addition the crystal structure of HTTA has been determined. Radical cations obtained by one electron oxidation of the dihydropyrazines have been characterized by electron spin resonance spectroscopy.

Introduction

The 1,4-dihydropyrazine unit is important in nature as a component of the flavin coenzymes[1] and several marine luciferins.[2,3] The stability of three different oxidation states makes these molecules interesting as electron donors in conducting charge transfer complexes and magnetic materials. Since 1,4-dihydropyrazine itself is unknown, various substitutions of the ring system are required to produce stable isolable molecules. This has been achieved with electron withdrawing and organometallic[4] substituents on nitrogen and bulky, conjugated substituents in other locations.[5–8] The resulting molecules have a variety of properties depending on the substituents and the planarity of the dihydropyrazine ring.[4,7] We have synthesized the molecule DDTTA where the dihydropyrazine nucleus is stabilized with ester groups at the 2 and 5 positions and a tertiary alkyl substituent on nitrogen.[9] This molecule features a planar central ring and displays unusual absorption in the visible region. We now report the synthesis of several stable analogues of this structure and their spectroscopic properties.

Results

DDTTA was synthesized by self condensation of 5,5-dimethyl-3-chloromethyl-5,6-dihydro-1,4-oxazin-2-one as previously described.[9] A similar procedure was used to synthesize the methyl amide analogue 2,4,4,6,8,8-hexamethyl-3,4,7,8-tetrahydro-2,4a,6,8a-tetraazaanthracene-1(2*H*),5(6*H*)-dione (HTTA) (Scheme 1). Thus 1,2-diamino-2-methylpropane condensed with ethyl pyruvate in toluene to give 5,6-dihydro-3,6,6-trimethylpyrazin-2(1*H*)-one **1** and 5,6-dihydro-3,5,5-trimethylpyrazin-2(1*H*)-one **2**.[10,11] The two regioisomers were separated by recrystallization or sublimation. Alkylation of **2** with sodium hydride and methyl iodide produced 5,6-dihydro-1,3,5,5-tetramethylpyrazin-2(1*H*)-one **3**.[10] Pyrazinone **3** was smoothly chlorinated with *tert*-butyl hypochlorite in dichloromethane and the resulting chloromethyl pyrazinone **4** underwent self condensation in the presence of diisopropylethylamine in dimethylformamide to give HTTA in 16% yield. Though chlorination of pyrazinone **2** also proceeded smoothly, attempts at self condensation to produce a dihydropyrazine were unsuccessful. Thioxo derivatives DDTTA–S and DDTTA–S_2 were synthesized by reaction of DDTTA with phosphorus pentasulfide (P_2S_5) in pyridine (Scheme 2) and separated by column chromatography on silica gel. Attempts at thionation of HTTA with P_2S_5 or Lawesson's reagent resulted only in the oxidation of HTTA.



Scheme 1

Crystals suitable for X-ray crystallography were obtained for HTTA. The crystal structure reveals a planar central ring, though the pyrazine nitrogens have a distinctly pyramidal geometry with the sum of the bond angles for N(1) equal to

Table 1 Selected bond lengths and angles for HTTA and DDTTA. The atom numbering scheme is shown in Fig. 1.

	Bond lengths/Å			Bond angles (°)	
	HTTA	DDTTA		HTTA	DDTTA
N(1)–C(1)	1.386(2)	1.351(2)	C(1)–N(1)–C(2)	114.10(13)	116.3(1)
N(1)–C(2)	1.434(2)	1.443(1)	C(2)–C(1)–N(1)	124.3(2)	123.9(1)
C(1)–C(2)	1.354(2)	1.343(2)	N(1)–C(2)–C(1)	121.30(15)	119.5(1)
N(1)–C(5)	1.482(2)	1.476(2)	C(1)–N(1)–C(5)	120.74(13)	123.2(1)
			C(2)–N(1)–C(5)	115.07(13)	117.7(1)

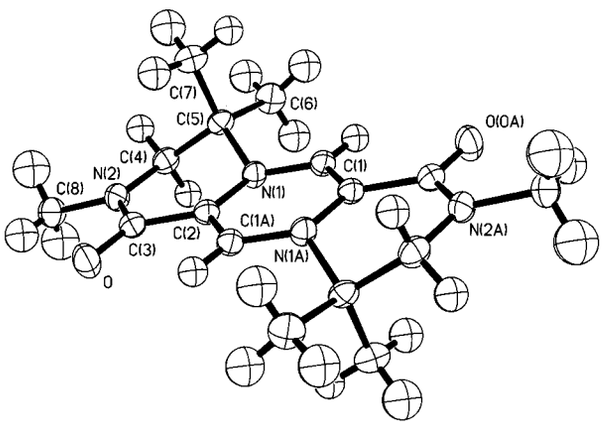
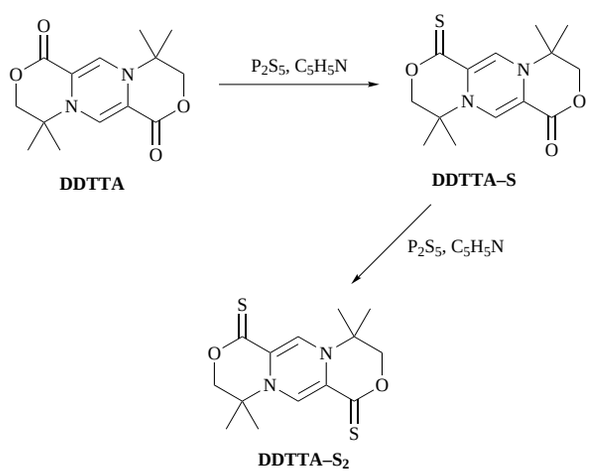


Fig. 1 Thermal ellipsoid plot for HTTA showing atomic numbering scheme used for the structure solution and refinement. Ellipsoids are drawn at the 50% probability level.



Scheme 2

349.91°. A thermal ellipsoid plot for HTTA is depicted in Fig. 1. Significant bond lengths and angles for HTTA are reported in Table 1 along with previously reported values for DDTTA. Crystal data and data collection parameters are given in Tables 2 and 3.† The structure solution and refinement are summarized in Table 4.

Like DDTTA, all three new dihydropyrazines showed a symmetry forbidden π–π* transition in the visible region. Values for λ_{max} and extinction coefficients for the new molecules and DDTTA are compared in Table 5. DDTTA–S and DDTTA–S_2 also showed a strong absorption at 408 and 500 nm, respectively, resulting from the thioxo ester group.

† Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available *via* the RSC Web pages (http://www.rsc.org/perkin1). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/165.

Table 2 Crystal data for $C_{16}H_{24}N_4O_2$

Empirical formula	$C_{16}H_{24}N_4O_2$
Formula mass	304.39
Crystal size, mm	0.231 × 0.062 × 0.062
Crystal color, habit	purple parallelepiped
Crystal system	monoclinic
Space group	$P2_1/n$
a	5.9432(4) Å
b	13.0525(8) Å
c	10.2325(6) Å
α	90°
β	97.1600(10)°
γ	90°
Volume	787.58(9) Å^3
Z, formula units/cell	2
Density (calculated)	1.284 Mg m^{-3}
Absorption coefficient	0.087 mm^{-1}
F(000)	328
Absorption correction	none
Range transmission coefficients	0.99 and 0.98

Table 3 Data collection parameters for $C_{16}H_{24}N_4O_2$

Diffractometer	Siemens SMART
T/K	168(2)
Radiation source	sealed tube
λ/Å	0.710 73 Mo-Kα
Monochromator	graphite
Cell measurement	
Reflections used	3945
θ range	27.49 < θ < 31.50
θ range, data collection	2.54 < θ < 27.49
Scan type	ω scans
Index ranges	$-8 \leqslant h \leqslant 8$, $-18 \leqslant k \leqslant 18$, $-14 \leqslant l \leqslant 14$
Reflections collected	8391
Independent reflections	1816 [R(int) = 0.0492]
Standard reflections	50 frames re-measured
Stability of standards	no decay observed

Table 4 Structure solution and refinement for $C_{16}H_{24}N_4O_2$

System used [12,13]	Siemens SHELXTL
Structure solution	direct
Data/restraints/parameters	1793/0/148
Hydrogen atoms	Full refinement
Weighting scheme	calc. $w^{-1} = [\sigma^2(F_o^2) + (0.0271P)^2 + 0.5248P]$ where $P = (F_o^2 + 2F_c^2) \div 3$
Final R indices[a] [$I > 2\sigma(I)$]	$R1 = 0.0499$, $wR2 = 0.0990$
Reflections observed	1391
R indices (all data)	$R1 = 0.0744$, $wR2 = 0.1142$
Goodness-of-fit[b] on F^2	1.087
Largest diff. peak and hole	0.278 and −0.174

[a] $R1 = \dfrac{\Sigma\|F_o| - |F_c\|}{\Sigma|F_o|}$; $wR2 = \sqrt{\dfrac{\Sigma[w(F_o^2 - F_c^2)^2]}{\Sigma[w(F_o^2)^2]}}$;

[b] GOF = $S = \sqrt{\dfrac{\Sigma[w(F_o^2 - F_c^2)^2]}{(M - N)}}$ where M is the number of reflections and N is the number of parameters refined.

Cyclic voltammetry of all three species showed a quasi-reversible initial oxidation to give the radical cation and subsequent oxidation at higher potential to give the dication. The latter reaction was reversible only with the amide. Oxidation potentials are listed in Table 6.

HTTA was readily hydrogenated with H_2 and Pd–C in methanol to give the tetrahydropyrazine **5**. Unlike the hydrogenated DDTTA analogue,[9] **5** is not easily re-oxidized.

Solutions of the radical cations were generated by oxidation of the respective dihydropyrazines with one equivalent of Fe(phen)$_3^{3+}$ in acetonitrile. Identical ESR spectra were observed for all three molecules with $g = 2.0035$ and a hyperfine coupling of 0.71 mT to two equivalent nitrogen atoms. Coupling to hydrogen was not observed.

Table 5 Spectroscopic data for DDTTA, HTTA, DDTTA–S and DDTTA–S_2

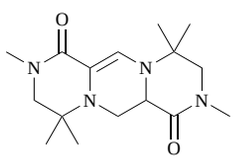
	λ_{max}/nm[a]	ε/M^{-1} cm^{-1}	Color of solution
DDTTA	572	118	blue
DDTTA–S	708	1160	green
DDTTA–S_2	658	340	greenish red
HTTA[b]	526	100	red

[a] Spectra were recorded in acetonitrile unless otherwise noted. [b] Spectrum recorded in methanol; HTTA is sparingly soluble in acetonitrile.

Table 6 Electrochemical data for DDTTA, HTTA, DDTTA–S and DDTTA–S_2

	$E_1^{0'}$/V[a]	$E_2^{0'}$/V[b]
DDTTA	−0.31	0.6
DDTTA–S	−0.31	0.8[c]
DDTTA–S_2	−0.22	—
HTTA	−0.5	0.4

[a] Potential for the reduction $M^{\bullet+} + e^- \longrightarrow M$, measured *vs.* internal ferrocene/ferricinium in dichloromethane tetrabutylammonium perchlorate as electrolyte. [b] Potential for the reduction $M^{2+} + e^- \longrightarrow M^{\bullet+}$ under the same conditions. [c] Partially reversible.



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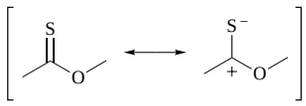
Discussion

DDTTA and its analogues possess a unique, visible chromophore resulting from a symmetry forbidden π–π* transition. The symmetry forbidden nature of the transition was first postulated on the basis of molecular orbital calculations[9] and is demonstrated by the increase in extinction coefficient upon replacing one carbonyl oxygen by sulfur and the subsequent decrease when the second carbonyl oxygen is replaced.

The series of molecules also demonstrates that the electron withdrawing substituents are, at least in part, responsible for the stability of these molecules. The effects of substituent changes can be understood as a competition between the effects of push–pull resonance and antiaromatic conjugation. The former occurs between the electron donating nitrogen lone pair on the pyrazine ring and the electron withdrawing carbonyl or thiocarbonyl groups and tends to produce delocalization and increased stability. Antiaromatic conjugation results from the interaction of the two lone pairs and two double bonds. Antiaromatic conjugation is a destabilizing effect which tends to localize the π system and distort the molecule from a planar conformation. The amide groups in HTTA are less effective in stabilizing push–pull resonance structures than esters. The effects of antiaromatic conjugation are then more pronounced, resulting in a more localized system with pyramidal pyrazine nitrogen atoms and discrete double bonds. Despite this increased localization, HTTA still has significant antiaromatic character as demonstrated by the ^{1}H NMR spectrum. Upon reduction of one double bond to form tetrahydropyrazine **5**, the remaining vinylic proton is shifted downfield by 0.71 ppm with respect to HTTA. Such paratropic shifts are indicative of a conjugated $4n$ π electron system.[14,15]

The effect of the thioester group on the dihydropyrazine ring is surprising. The first oxidation potentials of both DDTTA–S and DDTTA–S_2 are not significantly different from DDTTA despite the considerably lower electronegativity of sulfur. This probably results from the contribution of the resonance as shown in Scheme 3. This resonance is more significant in



Scheme 3 Thiocarbonyl resonance

thioesters than esters because of the poor C–S π overlap. The increased cationic character of the thiocarbonyl carbon results in the thioester group being almost as electron withdrawing as an ester. Past results have demonstrated that thiocarbonyl compounds are significantly stabilized by electron donating groups.[16] When DDTTA–S and DDTTA–S_2 radical cations are oxidized to the dication, the electron donating nature of the dihydropyrazine ring is removed and the molecules become unstable. This results in the irreversible/partially reversible oxidation observed in the cyclic votammetry experiment.

Conclusion

Analogues of the 1,4-dihydropyrazine DDTTA have been synthesized with the dihydropyrazine ring stabilized by thioester and amide electron withdrawing groups. All analogues show the same visible chromophore, though the detailed properties of the pyrazine ring are strongly dependent upon the electron withdrawing group.

Experimental

General

NMR spectra were recorded on a Varian VXR-300S, 300 MHz Fourier transform spectrometer and referenced to the chemical shift of residual protons in the deuterated solvent. Coupling constants are reported in Hz. Samples for IR spectra were dispersed in KBr pellets and spectra were recorded on a Perkin-Elmer 1600 model Fourier transform spectrometer. Mass spectra were recorded on a VG7070-EQ instrument; high resolution mass spectra were calibrated with a perfluoroketone mixture. Cyclic voltammetry was recorded on a Cypress CYSY-1 computer controlled electroanalysis system with an Ag/Ag^+ reference electrode, a platinum wire auxiliary electrode and a platinum disc working electrode. Nitrogen purged dichloromethane was used as solvent and tetrabutylammonium perchlorate as supporting electrolyte. Reduction potentials were measured relative to internal ferrocene/ferricenium and converted to normal hydrogen electrode (NHE) by adding 0.4 V. EPR spectra were recorded on a Bruker ESP300E X band spectrometer. Solutions containing radical cations were prepared by oxidation with ferrin [$Fe(phen)_3^{3+}$] in acetonitrile using techniques previously described for DDTTA.[9] DDTTA and 5,6-dihydro-1,3,5,5-tetramethylpyrazin-2(1*H*)-one were synthesized as previously described.[9,10] Because of their air sensitive nature, acceptable elemental analyses of HTTA, DDTTA–S and DDTTA–S_2 could not be obtained. Purity was estimated by thin layer chromatography (TLC) on silica gel plates.

3-(Chloromethyl)-5,6-dihydro-1,5,5-trimethylpyrazin-2(1*H*)-one

5,6-Dihydro-1,3,5,5-tetramethylpyrazin(1*H*)-one (6.86 g, 45 mmol) was dissolved in dichloromethane (50 cm^3) and the solution cooled to 0 °C in an ice bath under nitrogen. *tert*-Butyl hypochlorite (4.88 g, 45 mmol) in dichloromethane (20 cm^3) was added dropwise in the dark and the solution stirred at 0 °C for 1.5 h. Evaporation of the volatile materials gave the crude product as a reddish oil (9.01 g, 99%) with $\delta_H(CDCl_3)$ 4.37 (s, 2H, CH_2), 3.28 (s, 2H, CH_2), 3.02 (s, 3H, NMe), 1.27 (s, 6H, 2 CH_3); $\delta_C(CDCl_3)$ 157.9, 155.2, 56.7, 55.1, 42.5, 34.7, 26.1 (2 C); the material was unstable and could not be purified sufficiently for elemental analysis. The crude product was used directly in the synthesis of HTTA.

2,4,4,6,8,8-Hexamethyl-3,4,7,8-tetrahydro-2,4a,6,8a-tetraazaanthracene-1(2*H*),5(6*H*)-dione (HTTA)

Freshly prepared 3-(chloromethyl)-5,6-dihydro-1,5,5-trimethylpyrazin-2(1*H*)-one (9.00 g, 0.05 mol) was dissolved in dimethylformamide (40 cm^3) and diisopropylethylamine (6.2 g, 0.05 mol) added. The solution was heated under a nitrogen atmosphere at 90 °C for 15 h. Evaporation gave a black sludge which was stirred with 100 cm^3 water and filtered. The solid residue was washed with 100 cm^3 of toluene to give a yellowish-violet solid. This was transferred to a glove bag and washed with acetone (20 cm^3) and acetonitrile (20 cm^3) under a nitrogen atmosphere to leave 1.19 g (16%) HTTA as a purple solid, pure by TLC under a nitrogen atmosphere (7:3 EtOAc–CH_2Cl_2, R_f 0.67) with δ_H([$^2H_5$]pyridine) 6.60 (s, 2H, 2 CH), 2.91 (s, 6H, 2 CH_3), 2.86 (s, 4H, 2 CH_2), 1.12 (s, 12H, 4 CH_3); δ_C([$^2H_5$]pyridine), 23.05, 34.87, 51.73, 59.07, 117.5, 127.35, 160.04; ν_{max}(KBr)/cm^{-1} 1638 (C=O), 1593 (C=C); *m*/*z* (EI, 70 eV) 304 (M, 100%), 289 (27), 261 (21), 56 (48), 55 (43); λ_{max}(MeOH)/nm 308 (ε/dm^3 mol^{-1} cm^{-1} 6500), 526 (100).

Single crystals of HTTA were grown by layering a dichloromethane solution with *n*-heptane and allowing the layers to diffuse together under a nitrogen atmosphere. The resulting small purple parallelepipeds were used for structure determination. Full details of data collection and refinement are given in Tables 3 and 4.

3,4,7,8-Tetrahydro-4,4,8,8-tetramethyl-5-thioxo-2,6-dioxa-4a,8a-diazaanthracen-1-one (DDTTA–S) and 3,4,7,8-tetrahydro-4,4,8,8-tetramethyl-2,6-dioxa-4a,8a-diazaanthracene-1,5-dithione (DDTTA–S_2)

DDTTA (578 mg, 2 mmol) and phosphorus pentasulfide (1 g, 0.5 mmol) were combined in dry pyridine (50 cm^3) under nitrogen and heated under reflux for 12 h. The resultant mixture was poured into dichloromethane to precipitate phosphorus compounds, and filtered. The filtrate was evaporated and redissolved in nitrogen purged dichloromethane. The dichloromethane solution was applied to a silica gel column and eluted with nitrogen purged 7:3 ethyl acetate–dichloromethane. A continuous stream of nitrogen was passed over the collected eluent. Evaporation of the solvent gave the dithione (DDTTA–S_2) as 50 mg of a reddish-green crystalline solid, pure by TLC (7:3 EtOAc–CH_2Cl_2, R_f 0.32), with δ_H($CDCl_3$) 7.63 (s, 2H, 2 CH), 3.88 (s, 4H, 2 CH_2), 1.39 (s, 12H, 4 CH_3); ν_{max}(KBr)/cm^{-1} 1550 (C=C); *m*/*z* (EI, 70 eV) 310 (M^+, 100%), 194 (50), 149 (95), 131 (58), 169 (42) (Found: M^+, 310.0822; calc. for $C_{14}H_{18}N_2O_2S_2$: *M*, 310.0810); λ_{max}(CH_3CN)/nm 224 (ε/dm^3 mol^{-1} cm^{-1} 9320), 236 (8630), 264 (4188), 342 (1370), 500 (30 700), 648 (340). Further elution of the silica gel column gave unreacted DDTTA. Finally, elution with nitrogen purged acetone gave 10 mg of the bright green monothione (DDTTA–S), pure by TLC (7:3 EtOAc–CH_2Cl_2, R_f 0.1), with δ_H($CDCl_3$) 7.45 (s, 1H, CH), 6.61 (s, 1H, CH), 3.83 (s, 2H, CH_2), 3.77 (s, 2H, CH_2), 1.36 (s, 6H, 2 CH_3), 1.25 (s, 6H, 2 CH_3); ν_{max}(KBr)/cm^{-1} 1686 (C=O), 1560 (C=C); *m*/*z* (EI, 70 eV) 294 (M^+, 100%), 178 (68), 151 (25) (Found: M^+, 294.1043; calc. for $C_{14}H_{18}N_2O_3S$: *M*, 294.1038); λ_{max}(CH_3CN)/nm 228 (ε/dm^3 mol^{-1} cm^{-1} 23 700), 328 (8560), 408 (36 200), 708 (1160).

2,4,4,6,8,8-Hexamethyl-3,4,7,8,9,9a-hexahydro-2,4a,6,8a-tetraazaanthracene-1(2*H*),5(6*H*)-dione 5

HTTA (49 mg, 0.16 mmol) and palladium on carbon (5% Pd, 10 mg) were combined under a hydrogen atmosphere. Methanol (10 cm^3) was added in one portion and the mixture stirred vigorously. Stirring was continued until the solution faded from purple to colorless (~3 h). The solution was filtered through a Celite pad and evaporated to leave 47 mg (95%) of **5** as a white solid. This had δ_H(C_6D_6) 7.30 (s, 1H, CH), 4.0 (m, 2H, AB portion of deceptive ABX pattern), 3.07 (m, 1H, X portion of deceptive ABX pattern), 2.8 (d, 1H, *J* 12), 2.77 (s, 3H), 2.54 (s, 3H), 2.41 (d, 1H, *J* 12), 2.27 (d, 1H, *J* 12), 2.04 (d, 1H, *J* 12), 0.85 (s, 3H), 0.82 (s, 3H), 0.76 (s, 3H), 0.74 (s, 3H); δ_C($CDCl_3$) 166.5, 162.0, 119.3, 115.3, 60.4, 59.4, 54.6, 52.8, 52.0, 44.4, 34.8, 34.5, 24.9, 23.9, 22.5, 18.3; ν_{max}(KBr)/cm^{-1} 1647 (C=O), 1598 (C=C); *m*/*z* (EI, 70 eV) 306 (M^+, 16%), 305 (23), 304 (100), 289 (38), 261 (34), 191 (60), 55 (60), 42 (55); λ_{max}(MeOH)/nm 210 (ε/dm^3 mol^{-1} cm^{-1} 8900) 324 (4100). The sample was recrystallized from dichloromethane–heptane for analysis and gave a 3:1 dichloromethane solvate [Found: C, 58.46; H, 8.0; N, 16.91; calc. for $(C_{16}H_{26}N_4O_2)_3 \cdot CH_2Cl_2$: C, 58.61; H, 8.03; N, 16.74%].

Acknowledgements

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