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Conformationally stressed phthalocyanines: the non-planarity of the 1,4,8,11,15,18,22,25-octaisopentyl derivative

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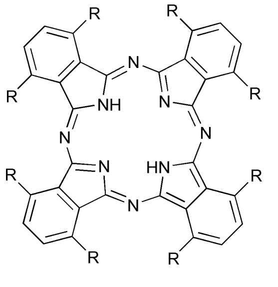
An X-ray crystal structure determination reveals that 1,4,8,11,15,18,22,25-octaisopentylphthalocyanine adopts a saddle conformation, a geometry which shows modified spectroscopic properties and reduced photostability relative to planar ring structures.

Phthalocyanines (Pcs) are important commercial dyes and pigments[1] but their interesting photophysical and conducting properties[2] also render them suitable for a number of 'high-tech' applications. Examples are used as charge carriers in photocopiers, as dyes in laser/LED printing[3] and as laser light absorbers for optical data storage systems.[4] Others are promising candidates for exploitation in devices such as solar cells,[5] gas sensors[6] and optical limiters[7] and, in medicine, as singlet oxygen photosensitizers for photodynamic therapy (PDT)[8] and as a therapy for transmissible spongiform encephalopathies.[9] Such developments have benefited from the ease of tuning or modifying the properties of the ring system. Principal strategies involve ring substitution and incorporation of a metal ion or metalloid element at the centre of the ring. However, the effect of ring conformation on properties has not been adequately addressed, a situation in marked contrast with studies of ring distortion of the related porphyrin[10] and tetrabenzoporphyrin[11] systems. X-Ray structure determinations[12] show that **1** is essentially planar, allowing maximum delocalisation of the π electron system. Analogues of **1** metallated with first row transition metal ions are similar but larger metal ions, *e.g.* Pb and Sn, distort the geometry.[12] The present paper is concerned with the use of substituents alone to distort ring geometry through conformational stress. Previous X-ray studies on substituted Pcs, though few,[12] include those for two non-peripherally substituted metal-free derivatives, **2**[13] and **3**.[14] The macrocyclic cores show some limited distortion from planarity, *vide infra*, but potential conformational stress involving substituents is largely relieved through the location of some of them orthogonal to the ring. Here we report results for **4**,[15] an octaalkyl derivative in which the point of branching of the chain is one bond closer to the core than in **3**. The greater steric congestion leads to a saddle shaped conformation of the ring without precedent in the published literature on non-metallated Pc derivatives.[16] Solution phase spectroscopic properties and photostability of **4** are compared with those of **2** and the straight chain isomer of **4**, *viz.*, **5**.



1 $R = H$
2 $R = (CH_2)_5CH_3$
3 $R = O(CH_2)_2CH(CH_3)_2$
4 $R = (CH_2)_2CH(CH_3)_2$
5 $R = (CH_2)_4CH_3$

DSC analysis of **4**, recrystallised from THF–MeOH, indicated there is a crystal to crystal transition at 263 K. The X-ray crystal structure of **4**† at rt shows that the compound crystallises in the centrosymmetric space group *C*2/*c*. The asymmetric unit consists of half a molecule with the other half being generated by a 2-fold rotation axis. However, there is disorder in the positions of some of the atoms in the alkyl chains and evidence of considerable thermal motion. An attempt to model the disorder better by determining the crystal structure at low temperature was thwarted by the structural phase transition at 263 K. On approaching this temperature the crystal began to lose integrity as shown by smearing out of the diffraction spots into arcs.

The rt data reveal unambiguously that the central core of the molecule deviates markedly from planarity forming a saddle shape, Fig. 1a and 1b. The dihedral angles between the pair of planes formed by the isoindole units on either side of the core are both 32.0°. The two crystallographically distinct five membered rings make angles at 18.0 and 11.3° with the mean plane generated by the four pyrrole type nitrogens. The calculated positions of the hydrogen atoms attached to nitrogen are therefore out of this plane. The molecules pack together to form stacks, Fig. 1b, which run along the crystallographic *c* axis. This involves a number of π-stacking interactions, the shortest of which is 3.686 Å. The ring conformation of **4** differs significantly from that adopted by **2**,[13] shown in Fig. 1c for comparison. Here isoindole units on opposite sides of the ring are located in parallel planes. The distances between one pair of planes is 0.3 Å, for the other it is 0.15 Å.

Table 1 includes spectroscopic data for **2**, **4** and **5**. Comparison of those for **2** and **4**, the two compounds for which crystal structure data are now available, shows there are clear differences. In particular, the visible region absorption bands, Q_x and Q_y, of **4** show a bathochromic shift and lowering of the extinction coefficient relative to those of **2.** This is consistent with the trend detected upon distortion from planarity of the 18 π electron system of porphyrins[10] and indicates that the non-planar structure of **4** persists in the solution phase.

^{1}H-NMR spectral data obtained from dilute solutions at 50 °C, conditions devised to limit aggregation, show that the N-*H* signal of **4** is to lower field than for **2**. This may point to differences in the degree of aggregation for the two compounds and/or indicate a weaker ring current in **4** attributable to the greater departure of the cyclic π electron system from planarity. ^{1}H-NMR spectra of **4** recorded down to -70 °C in THF-d_8 solution showed broadening and separation of two sets of signals for the benzylic protons. However, there is no coupling between them and we therefore assign the phenomenon to slowing of N–H tautomerism rather than slowing of conformational inversion of a saddle structure for the ring itself. The latter would render the CH_2 protons diastereotopic.

Spectral data for **5** are more similar to those of **2** than **4**. The Q-band extinction coefficient and shielding of the N–H protons is highest for **5** and offers an indication that the core of **5** may be the least distorted of all three compounds. The data highlight the potential for using spectroscopic parameters for assessing Pc ring conformation in the solution phase.

Phthalocyanines are known to undergo photooxidative cleavage, particularly in the solution phase, leading to phthalimide derivatives.[17] Though a potential problem for the use of these compounds in devices, photobleaching of Pc photosensitizers in PDT treatment may provide a means of facilitating their removal from patients. Photobleaching of **2**, **4** and **5** as solutions

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Table 1 Comparative spectroscopic and photodecomposition data for compounds **2**, **4** and **5**.

Solvent or medium	Parameter	Compound **2**	Compound **4**	Compound **5**
THF	$\lambda_{\max}$ Q_x ($\varepsilon \times 10^{-5}$)[a]	728 nm (1.68)	731 nm (1.55)	728 nm (1.77)
THF	$\lambda_{\max}$ Q_y[a]	696 nm (1.47)	701 nm (1.34)	696 nm (1.54)
KBr disc	ν_{N-H}	3297 cm^{-1}	3302 cm^{-1}	3297 cm^{-1}
$CHCl_3$	ν_{N-H}	3308 cm^{-1}	3310 cm^{-1}	3308 cm^{-1}
10^{-3}M, C_6D_6	δ_{N-H} (50 °C)	−0.148 ppm	−0.052 ppm	−0.165 ppm
THF	rel. k $_{\text{(photodecomp.)}}$[b]	1.13	1.43	1.00

[a] ε values were obtained from the Beer–Lambert plots over the concentration range 5×10^{-7} to 5×10^{-5}M. The plots remained linear up to 1×10^{-4} M. [b] Relative pseudo first order rates of photodecomposition in aerated solutions of compounds upon irradiation using UV lamps, starting molarity 10^{-5} M.

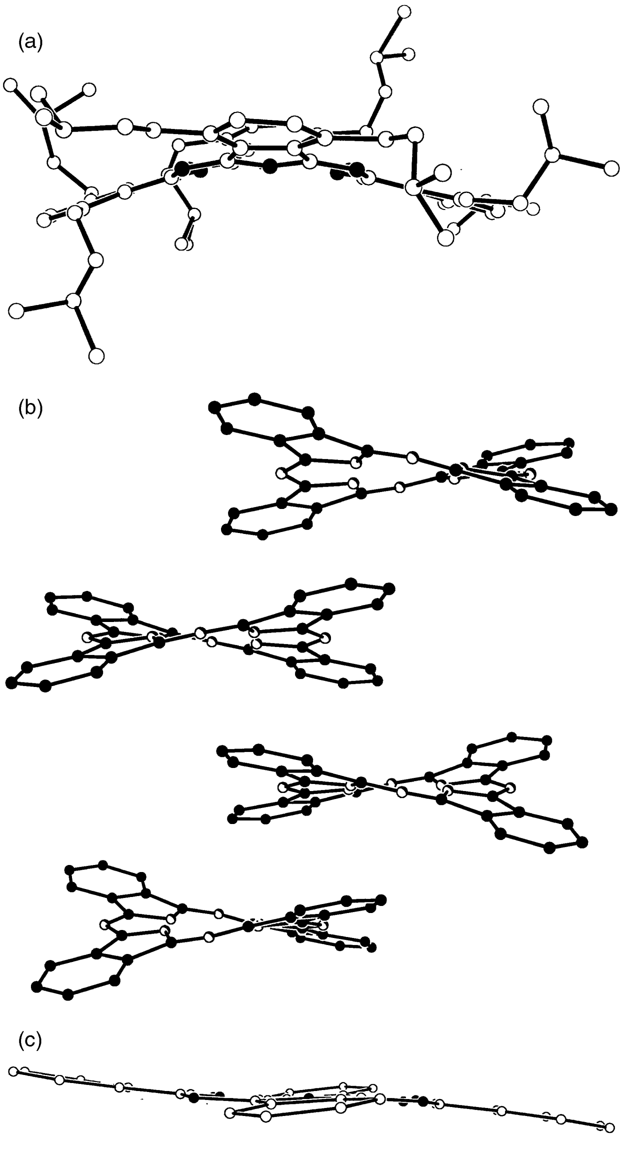

Fig. 1 (a) Representation of the molecular structure of 1,4,8,11,15,18,22,25-octaisopentylphthalocyanine, **4**. (b) The structure with the alkyl chains removed for clarity and illustrating the stacking of the molecules within a column. (c) A view of the ring conformation of compound **2**[13] with the hexyl groups removed.

in THF was monitored by the disappearance of the Q-band on UV irradiation (S.Y.L.V.A.N.I.A. Blacklight-blue, 8 W), (Table 1). The consumption of compound followed first order kinetics with the rate of photobleaching slowest for **5** and fastest for **4**. This is likely to be a further manifestation of the significant ring distortion of **4**.

In conclusion, the work demonstrates that the conformation of the Pc ring can be adjusted by judicious choice and location of substituents leading to a concomitant fine tuning of spectroscopic properties and photochemical stability.

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Notes and references

† Crystal data for $C_{72}H_{98}N_8$: M = 1075.58, monoclinic, $C2/c$, a = 20.433(5), b = 33.873(4), c = 10.025(4) Å, β = 110.12(2)°, Z = 4, ρ_{calcd} = 1.097 Mg m^{-3}, 10287 reflections were collected of which 5349 were unique (R_{int} = 0.584), $2\theta_{\max}$ = 51.02°, graphite-monochromated Mo-kα radiation (λ = 0.71073 Å). Data were collected using a Rigaku R-AXIS IIc area detector and corrected for Lorentz and polarisation factors but no absorption correction was applied (μ = 0.064 mm^{-1}). The structure was solved by direct methods (SHELXTL-PLUS) and refined using full-matrix least-squares on F^2 using SHELX-93 software. The hydrogen atoms associated with the ordered part of the molecule were placed on idealised positions and allowed to ride on their parent atoms, no hydrogens were placed on the disordered portion of the side chain. 384 parameters refined, $R1$ = 0.1073 for $F > 4\sigma(F)$, $wR2$ = 0.3911 for all data S = 0.939, maximum residual electron density (largest electron hole) 0.449 (−0.260) e Å^{-3}. CCDC 182/1786. See http://www.rsc.org/suppdata/cc/b0/b006935n/ for crystallographic files in .cif format.

1 F. H. Moser and A. L. Thomas, *The Phthalocyanines, Vol. 2 Manufacture and Applications*, CRC Press, Boca Raton, FL 1983.
2 *Phthalocyanines: Properties and Applications, Vols. 1-4*, ed. C. C. Leznoff and A. B. P. Lever, VCH Publishers, New York, 1989, 1993, 1996; N. B. McKeown, *Phthalocyanine Materials: Synthesis, Structure and Function*, Cambridge University Press, Cambridge, 1998.
3 P. Gregory, *J. Porphyrins Phthalocyanines*, 2000, **4**, 432.
4 D. Birkett, *Chem. Ind.*, 2000, 178.
5 H. Eichhorn, *J. Porphyrins Phthalocyanines*, 2000, **4**, 88.
6 J. D. Wright, *Prog. Surf. Sci.*, 1989, **31**, 1; A. W. Snow and W. R. Barger in *Phthalocyanines—Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH Publishers, New York, 1989, 341.
7 J. S. Shirk, R. G. S. Pong, S. R. Flom, H. Heckmann and M. Hanack, *J. Phys. Chem.*, 2000, **104**, 1438; G. de la Torre, P. Vázquez, F. Agulló-López and T. Torres, *J. Mater. Chem.*, 1998, **8**, 1671.
8 H. Hasrat and J. E. van Lier, *Chem. Rev.*, 1999, **99**, 2379.
9 S. A. Priola, A. Raines and W. S. Caughey, *Science*, 2000, **287**, 1503.
10 M. O. Senge, C. J. Medforth, T. P. Forsyth, D. A. Lee, M. M. Olmstead, W. Jentzen, R. K. Pandey, J. A. Shelnutt and K. M. Smith, *Inorg. Chem.*, 1997, **36**, 1149.
11 R.-J. Cheng, Y.-R. Chen, S. L. Wang and C. Y. Cheng, *Polyhedron*, 1993, **12**, 1353.
12 M. K. Engel, *Kawamura Rikagaku Kenkyusho Hokoku, (English)*, 1996, 11–54; *Chem. Abs.*, 1997, **127**, 313213.
13 I. Chambrier, M. J. Cook, M. Helliwell and A. K. Powell, *J. Chem. Soc., Chem. Commun.*, 1992, 444.
14 M. J. Cook, J. McMurdo and A. K. Powell, *J. Chem. Soc., Chem. Commun.*, 1993, 903.
15 N. B. McKeown, M. J. Cook and I. Chambrier, *J. Chem. Soc., Perkin Trans. 1*, 1990, 1169.
16 During the preparation of this paper, Dr N. B. McKeown, University of Manchester, UK, informed us of unpublished work on a hexadeca substituted Pc derivative which also adopts a saddle conformation.
17 A. K. Sobbi, D. Wöhrle and D. Schlettwein, *J. Chem. Soc., Perkin Trans. 2*, 1993, 481; M. J. Cook, I. Chambrier, S. J. Cracknell, D. A. Mayes and D. A. Russell, *Photochem. Photobiol.*, 1995, **62**, 542.