Unusual Conformational Stability of a Sterically Crowded Atropisomer of Methyl[α⁴-5,10,15,20-tetrakis(2′-phenylphenyl)porphyrinato]aluminium: a Possibility of CH–π Bonding Interactions in Organometallic Porphyrin Systems

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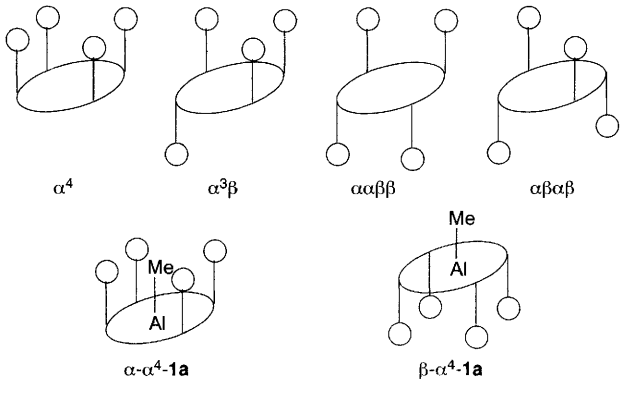
Through conformational studies on the topologically well-defined atropisomeric systems of organo-aluminium and -cobalt porphyrins, *e.g.* methyl[α⁴-5,10,15,20-tetrakis(2′-phenylphenyl)porphyrinato]aluminium (α⁴-**1a**), the presence of intramolecular CH–π bonding interactions are indicated between alkyl groups bonded to the central metal atoms and aromatic rings located at the *ortho* position of the *meso* phenyl substituents upon proximal orientation.

CH–π bonding interactions,[1] an attractive force operating between topologically proximate alkyl groups and aromatic rings, is a fundamental concept of non-bonding interaction in chemical and biological processes, which has been employed to account for unusual conformational behaviour of organic molecules,[2] stereoselectivities in enantioface-differentiating reactions,[3] molecular recognition modes in host–guest complexations,[4] and so forth. We wish to report here the first clear example of a prohibited conformational change resulting from intramolecular CH–π attractive forces in an atropisomeric system of an organometallic porphyrin.

5,10,15,20-Tetrakis(2′-phenylphenyl)porphyrin[5] has four possible atropisomers denoted as α⁴, α³β, αααββ, and αβαβ. When $AlMe_3$ is reacted with the α⁴-isomer, the resulting methylaluminium porphyrin α⁴-**1a** should have two isomers (α-α⁴, β-α⁴) with different degrees of steric crowing depending on the direction of the axial Me group. Each isomer could be selectively prepared by changing the amount of $AlMe_3$ charged. In the ^1H NMR spectra in C_6D_6, the β-α isomer showed a characteristic *Me*Al signal in the highly upfield region at δ −5.89 primarily due to the strong shielding effect of the porphyrin moiety, while the degree of upfield shift for the MeAl signal was more remarkable in the α-α isomer (δ −6.92) because of the additional shielding effect by the four proximate phenyl groups of the peripheral 2′-*phenyl*phenyl substituents.† When the sterically less crowded β-α⁴-**1a** was allowed to stand in C_6D_6 at 35° C, atropisomerization by rotation of the 2′-phenylphenyl groups around the phenyl group–porphyrin axis was observed to take place as shown in Fig. 1(*b*), where the population of the starting isomer, as determined by ^1H NMR, decreased to 68, 17 and 0% after 1, 6 and 8 h, respectively.‡ On the other hand, quite unexpectedly, the sterically crowded α-α⁴-**1a** underwent much slower atropisomerization under identical conditions, where the population of the starting isomer was >90% after 6 h, and 40% even after 50 h [Fig. 1(*a*)]. Atropisomerization starting from αααββ-**1a** proceeded at 35 °C in C_6D_6 initially giving α³β isomers [Fig. 2(*a*)]. Of interest was that the isomerization of αααββ-**1a** afforded α-α³β-**1a** [Fig.



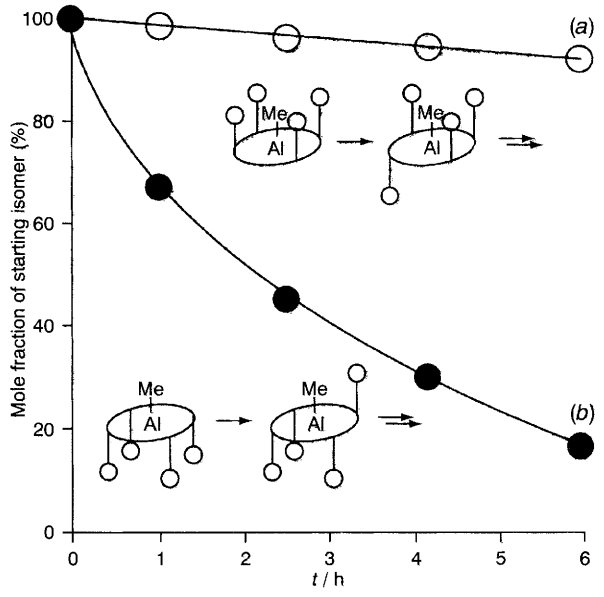


Fig. 1 Time-courses of atropisomerization of the α-α⁴ (*a*) and β-α⁴ (*b*) isomers of **1a** in C_6D_6 ($[\mathbf{1a}]_0$ = 0.02 mol dm^{-3}) at 35 °C under nitrogen. Mole fractions of the starting isomers, as determined by ^1H NMR.

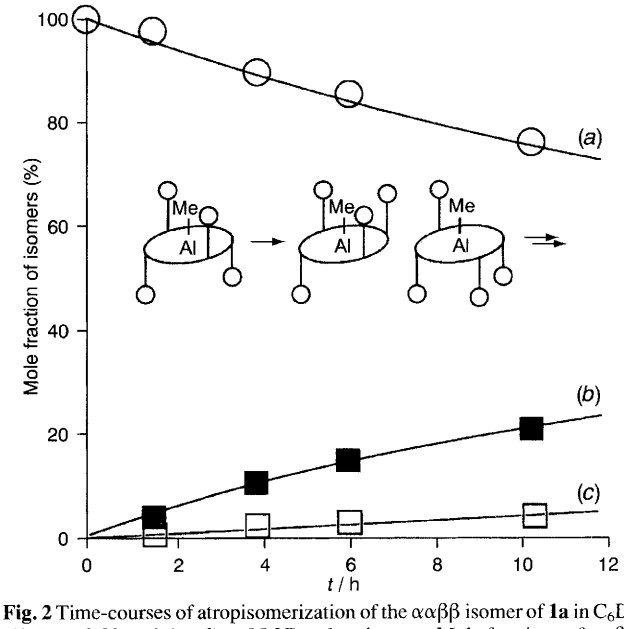


Fig. 2 Time-courses of atropisomerization of the αααββ isomer of **1a** in C_6D_6 ($[\mathbf{1a}]_0$ = 0.02 mol dm^{-3}) at 35 °C under nitrogen. Mole fractions of αααββ (*a*), α-α³β (*b*), and β-α³β (*c*) isomers, as determined by ^1H NMR.

2(*b*)] in preference to β-α^3β-**1a** [Fig. 2(*c*)], where the mole ratio of α-α^3β to β-α^3β isomer was 88:12 after 60% of the ααββ isomer had isomerized (50 h). The preferential isomerization into the more crowded isomer (α-α^3β-**1a**) was also observed in the isomerization from αβαβ-**1a** to α^3β-**1a**. These results indicate that the interaction such as CH–π interactions between the axial methyl group and the peripheral 2′-*phenyl*phenyl groups operates to make the sterically more hindered isomer structure more favourable.

In relation to this unexpected phenomena, methyl[5,10,15-triphenyl-20-(2′-phenylphenyl)porphyrinato]aluminium **2a**, a simpler homologue of **1a** carrying only one *ortho*-phenyl group, was prepared from 5,10,15-triphenyl-20-(2′-phenylphenyl)-porphyrin and $AlMe_3$. **2a** in C_6D_6 showed in its ^1H NMR spectrum two singlet MeAl signals at δ −5.97 and −5.84 due to the α-α and β-α isomers, respectively, where the integration of two characteristic signals indicated an isomer ratio of α-α to β-α of 64:36. This ratio remained unchanged throughout the observation at 35 °C for 32 h. Thus, the proximal orientation of the 2′-*phenyl*phenyl substituent to the Me–Al moiety was again much preferred to the distal orientation. In sharp contrast, the isomer ratio of the chloroaluminium complex (**2e**) was almost unity ([α-α]:[β-α] = 48:52). However, when the axial Cl atom of **2e** was replaced by methyl on treatment with MeLi,[6] the α-α to β-α isomer ratio reverted to 64:36. On the other hand, when the 2′-phenylphenyl group of **2a** was changed to 2′-methoxyphenyl group (**3a**), the distal orientation of the 2′-*methoxy*phenyl group to the Me–Al moiety (β-α) was even preferred by 10% to the proximal orientation (α-α) (45:55). The difference in conformational preference observed for **2a**, **2e** and **3a** strongly indicates the presence of CH–π bonding attractive forces in **2a** between the methyl group and the phenyl ring of the peripheral 2′-*phenyl*phenyl substituent. When an electron-donating 4″-MeO group was introduced on the 2′-phenyl group of **2a** (**8a**), the preference of the proximal orientation of the 2′-*phenyl*phenyl substituent to the Me–Al moiety was more pronounced ([α-α]:[β-α] = 72:28). On the other hand, an electron-withdrawing 4″-CF_3 group (**9a**) decreased the population of the proximal orientation ([α-α]:[β-α] = 58:43). The attractive force of CH–π bonding interaction possibly serves as a 'lock' to prohibit the conformational change of the crowded α-α^4 isomer of **1a** to relieve steric repulsion. The forces of CH–π bonding interaction and steric repulsion are actually the balancing factors which dominate the isomer ratio, as evidenced by the lower α-α isomer population for **2** having bulkier axial groups such as ethyl (**2b**, 59%), isobutyl (**2c**, 55%) and *n*-butyl (**2d**, 48%). The isomer ratio of these complexes remained unchanged at 35 °C for 24 h. Also of interest is the fact that the α-α to β-α isomer ratio of the methylcobalt complex **2f**, as determined by ^1H NMR ($CDCl_3$, 22 °C), was almost the same as observed for the aluminium analogue (**2a**), again indicating the presence of CH–π attractive forces between the methyl group bonded to the cobalt atom and the peripheral aromatic unit.

In conclusion, through conformational studies on the topologically well defined atropisomeric systems of organoaluminium and -cobalt porphyrins, the presence of *intra*molecular CH–π bonding interactions were indicated between alkyl groups bonded to the central metal atoms and aromatic rings located at the *ortho* position of the *meso* phenyl substituents upon proximal orientation.§

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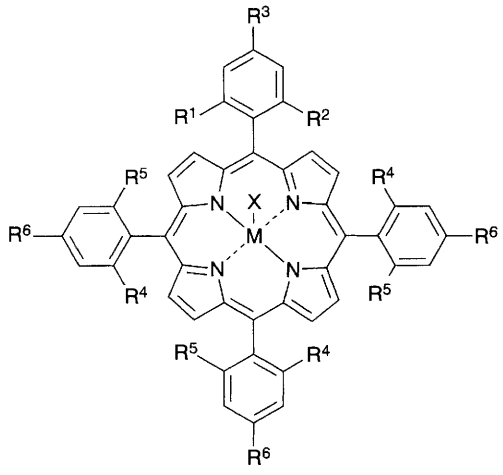

1 R^1 = Ph, R^2 = R^3 = H, R^4 = Ph, R^5 = R^6 = H
2 R^1 = Ph, R^2 = R^3 = R^4 = R^5 = R^6 = H
3 R^1 = OMe, R^2 = R^3 = R^4 = R^5 = R^6 = H
4 R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = Ph
5 R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = H
6 R^1 = R^2 = R^3 = Ph, R^4 = R^5 = R^6 = H
7 R^1 = R^2 = OMe, R^3 = R^4 = R^5 = R^6 = H
8 R^1 = C_6H_4OMe-*p*, R^2 = R^3 = R^4 = R^5 = R^6 = H
9 R^1 = $C_6H_4CF_3$-*p*, R^2 = R^3 = R^4 = R^5 = R^6 = H
a M = Al, X = Me
b M = Al, X = Et
c M = Al, X = Bu^i
d M = Al, X = Bu^n
e M = Al, X = Cl
f M = Co, X = Me

Footnotes

† The isomer structures were determined by reference to the ^1H NMR spectra in C_6D_6 of **4a** (CH_3Al: δ −7.06) and **5a** (−5.79).

‡ The populations of the isomers after 50 h were 0 (β-α^4), 11 (β-α^3β), 29 (αβαβ), 25 (ααββ), 32 (α-α^3β), and 3% (α-α^4), as determined by ^1H NMR.

§ A possibility of an intermolecular CH–π bonding interaction has been recently proposed in the site-specific coordination of aromatic bases with a zinc complex of picket fence porphyrins.[7]

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