Induced homohelicity of diphenimide bis-propellers†

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Letter

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Helicity correlation in switchable diphenimide bis-propellers results in their preferential homohelical, rather than heterohelical structures.

Molecular propellers of the general formula Ar_3X have been the subject of intense studies.[1–3] In such propellers the blades are planar aromatic rings connected to the central atom X. The chirality of the molecule arises from tilting the planar blades in the same direction. Examples include triarylboron,[4] triarylamine,[5] triphenylphosphine[6] and triarylmethane[7] propeller systems, as well as propeller chain systems.[8] However, far less studied molecular propeller systems are those having genuinely helical blades,[3] that is molecules or parts of them having a defined and same sense of helicity. Propeller molecules of fixed helicity find use as chiral ligands in asymmetric synthesis.[9]

A representative of molecular helical propellers with *switchable* helicity is the diphenimide molecule (DPI-H, **1**), a derivative of 2,2′-biphenyldicarboxylic acid. This C_2-symmetry molecule features a twisted biphenyl moiety and a seven-membered nonplanar (twist-boat) imide ring, which can be attached to any skeleton through a N–R bond. The two helical blades in the propeller are nonplanar benzoyl groups, each of them having the same helicity (Fig. 1).[10] X-Ray data on **1** show that the biphenyl moiety is twisted by $\omega = 33.9°$ and the helicity sense of the biphenyl and the two O=C-phenyl fragments is the opposite.[11]

Molecules having two adjacent diphenimide propellers represent a novel type of helical system. The two diphenimide propellers in each molecule can have either like (*P*,*P* or *M*,*M*) or unlike (*P*,*M*) helicity, which we propose to call accordingly *homohelical* or *heterohelical*. The proximity of the diphenimide propellers in molecules such as **3**–**5** should result in correlation of their helicity. In such a case, either homohelical or heterohelical molecules should be observed as conformationally preferred ones throughout the investigated series of compounds. Using a combination of spectroscopic, computational and X-ray diffraction methods we set out to determine if the helicity of bis-propellers **3**–**5** is correlated.

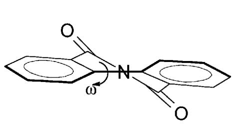
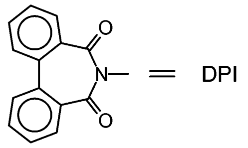


Fig. 1 Diphenimide as a molecular propeller with *M*-helically twisted blades. ω is the intra-ring angle between the planes of the benzene moieties.



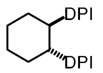
= DPI

1 DPI-H

2a DPI-(*R*)-CH(Me)-*cyclo*-C_6H_{11}

2b DPI-(*R*)-CH(Me)Ph

3



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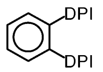
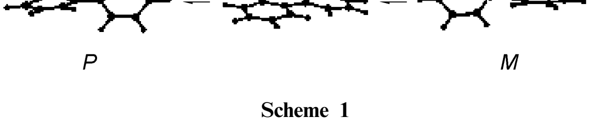


5 DPI-CH_2-DPI

In order to establish the helicity of bis-propellers **3**–**5**, we first embarked on elucidating the conformational and chiroptical properties of the simple propellers **1**, **2a** and **2b**. The barrier to helicity reversal in **1** is quite low. Full structure optimization of **1** by the DFT method employing the B3LYP functional and using a cc-pvdz basis set provided the biphenyl torsion angle $\omega = 38.3°$, in fair agreement with the X-ray data mentioned earlier. The optimized transition state for inversion of **1** is nearly planar, with a slightly pyramidalized imide nitrogen atom (Scheme 1). The calculated $\Delta G^{\#}$ at the B3LYP/cc-pvdz level is 16.0 kJ·mol^{-1} (3.82 kcal·mol^{-1}).

Chiral substituents attached to the nitrogen atom in **1** shift the propeller *P*/*M* equilibrium toward one of the two diastereomeric forms. Steric interactions are transmitted by the imide carbonyl groups that protrude in the direction of substituents located at the chiral α-carbon atom.

The optical activity of a diphenimide derived from (*S*)-phenylalaninol was studied by Schlögl *et al.*[12] On the basis of a PPP-SCF-CI MO calculation they concluded that the experimentally observed intense ^1B_b band (ε 90 000) at around 215 nm gives rise to a weak exciton couplet in the CD spectrum at 222 and 209 nm, which has negative rotatory power for a diphenimide structure of *P*-helicity. Our electronic absorption and chiroptical data on diphenimides **2**–**5** are significantly different. For example, both **2a** and **2b** display at ambient temperature strong Cotton effects at *ca.* 260 and 220 nm, that is within the diphenimide π-π* absorption band at 240 nm of



Scheme 1

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† Electronic supplementary information (ESI) available: full experimental and computational details. See http://www.rsc.org/suppdata/nj/b2/b207375g/.

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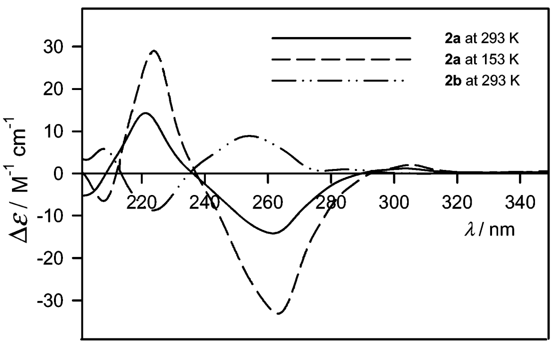

Fig. 2 CD spectra of **2a** (—) and **2b** (---) at 293 K in acetonitrile and of **2a** (–··) at 153 K in ethanol–methanol (4:1) solutions.

medium intensity (ε 25 000), as shown in Fig. 2. The Cotton effects of **2a** increase 2.5-fold on lowering the temperature from 293 K to 153 K in ethanol–methanol (4:1) solution. A free energy difference 0.9 kcal·mol^{-1} between the *M* and *P* propeller conformers of **2a** was obtained by a regression analysis of the variable-temperature CD data.[13]

Strikingly, the observed Cotton effects in **2a** and **2b** were of mirror symmetry, despite their having the same absolute configuration of the chiral substituent. Opposite-sign Cotton effects in **2a** and **2b** point to opposite helicity of the diphenimide chromophore, induced by steric demands of the chiral substituent. Molecular modelling (B3LYP/6-31G* method, Table 1) indeed confirmed the observed opposite propeller helicity preferences in **2a** (*P*) and **2b** (*M*), although the computed ΔE for **2a** (0.29 kcal mol^{-1}) is smaller than the 0.9 kcal mol^{-1} obtained from variable-temperature CD spectra.‡

In order to determine the preferred *P* or *M* helicities of the diphenimide propeller in **2a** and **2b** from the CD spectra, we first computed the energies and the transition polarization directions of the diphenimide chromophore using the CIS/cc-pvdz method on the B3LYP/cc-pvdz minimized C_2 symmetry structure of **1**. The results are shown in Fig. 3. We selected three transitions, the *x*-axis-polarized 290 nm transition (computed at 313 nm) and a pair of *x*,*z* polarized transitions belonging to the experimental absorption maximum at *ca.* 240 nm (computed at 234 and 212 nm, after wavelength correction, see Fig. 3).

The computed rotational strengths for *P*-**1** are positive for the 290 nm transition and negative/positive for the 260/220 nm CD bands. The rotatory strength of the former transition conforms to the general rule relating the sign of the rotational strength of B-type transitions to the helicity of the C_2-symmetry chromophore,[14] whereas the latter pair of transitions can be regarded as originating from exciton coupling.

It is therefore evident that for **2a** and **2b** the preferred diphenimide propeller helicities are correspondingly *P* and *M*, in agreement with the computed steric energies of the conformers (Table 1). X-Ray analysis of *rac*-**2b** (Fig. 4) revealed that in the crystal the *M* diphenimide propeller structure is associated with the *R* configuration at the chiral center, as it was found in solution by the analysis of the CD data.

In the case of bis-diphenimides **3**–**5** the steric energy differences between the conformers were obtained by single-point energy calculations at the B3LYP/6-31G* level of theory for the PM3 optimized structures (Table 1). In each case the computed homohelical bis-propeller structures were of lower energy, compared to the heterohelical ones.

Further evidence for the preferred homohelical bis-propeller structures was obtained from the X-ray analysis. In the crystal of **3** two independent diastereomeric *M*,*M* and *P*,*P* homohelical diphenimide molecules were present. The bis-diphenimide fragments in **4** and **5** were homohelical in the crystals, which form racemic compounds (see Table 1). The homohelicity of vicinally substituted bis-diphenimides seems to be stabilized by intramolecular face-stacking interactions: a considerable face-stacking effect was observed in **3** and **4**, as judged by a partial overlap of the benzene rings at a distance of *ca.* 3.5 Å (Fig. 4).

The ^{1}H NMR data from a solution of **3** provide additional evidence for the presence of two diastereomeric species. At room temperature both the aromatic and the cyclohexane CHN proton signals were broad due to conformational exchange. At 225 K in CDCl$_3$ solution two signals of equal intensity for the CHN protons were observed at δ 5.66 and

Table 1 Computed relative energies (ΔE) and biphenyl torsion angles (ω) of *P* and *M* molecular propellers

Compound	Conformer	ΔE/kcal mol^{-1}	Calcd ω^a/deg	Exptal ω^b/deg
2a	*P*	0	40.5	–[c]
	M	0.29	−40.6	–[c]
2b	*P*	2.31	40.9	42.6[d]
	M	0	−40.5	−42.6[d]
3	*P*,*P*	1.23	45.2	39.5, 44.9
	P,*M*	3.76	±45.4	–
	M,*M*	0	−45.5	−40.1, −44.5
4	*P*,*P*/*M*,*M*	0	46.1/−46.1	41.0, 42.4/−41.0, −42.4
	P,*M*	6.37	±46.0	–
5	*P*,*P*/*M*,*M*	0	45.8/−45.8	−37.2/−37.2
	P,*M*	7.81	±45.9	–

[a] Computed for **2a** and **2b** using the B3LYP/6-31G* method for the B3LYP/STO-3G* geometry and for **3**–**5** using the B3LYP/6-31G* method for the PM3 geometry. [b] X-Ray structure determination. [c] No data. [d] Data for *rac*-**2b**.

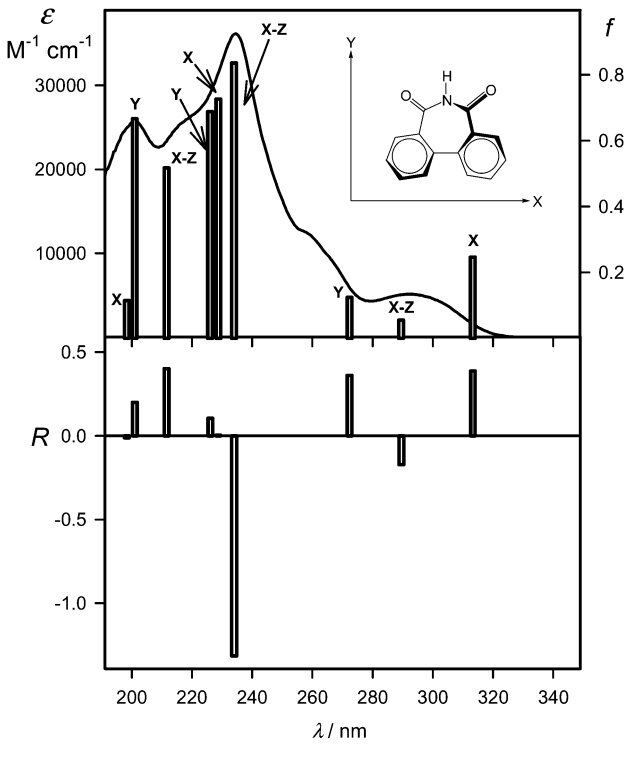

Fig. 3 Top: UV spectrum of **1** (—) in acetonitrile and computed (CIS/cc-pvdz) transitions of **1** with C_2 symmetry (vertical bars). The computed energies are multiplied by an empirical factor of 1.32 to account for electron correlation effects. Bottom: computed (CIS/cc-pvdz) rotatory strengths of the transitions of *P*-**1**.

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‡ The computed structures of the conformers of **2a**, **2b**, **3** and **5** have one of the imide C=O bonds nearly coplanar with the C–H bond at the nitrogen-bearing carbon atom.

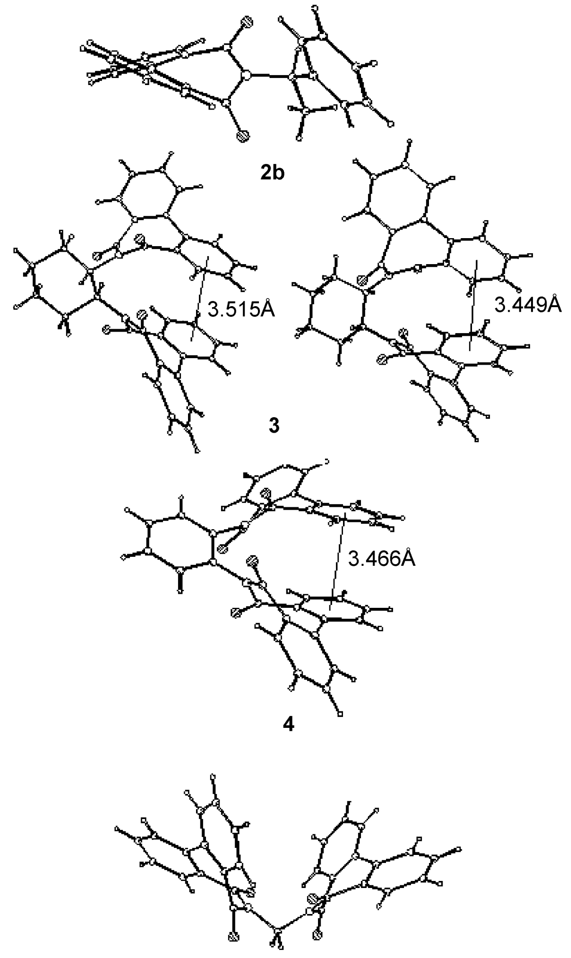

Fig. 4 Molecular structures of propellers **2b**, **3**, **4** and **5** determined by X-ray diffraction. Two independent molecules of diastereomeric structure, *M*,*M* (left) and *P*,*P* (right), are found in the crystal of **3**.

5.77. Further temperature lowering allowed to clearly distinguish the *M*,*M* and *P*,*P* propellers from the *P*,*M* species, as the signals displayed unequal intensity, the one downfield being approximately 60% more intense in CD_2Cl_2 solution at 193 K.

The CD spectrum of **3** is quite unusual, as it changes sign in the 230–280 nm region upon lowering the temperature (Fig. 5). The shape of the CD spectra is apparently made more complex by the effects of exciton interactions between the vicinal diphenimide chromophores. Assuming that these interactions have minor contributions to the observed Cotton effects the following rationalization can be offered. At room temperature the shape of the CD spectrum of **3** is similar to that of **2a**, that is the CD effect of the *P*,*P*-helical propeller of **3** dominates. On lowering the temperature the contribution due to the CD of the *M*,*M*-**3** helical propeller (which is of lower steric energy, see Table 1) progressively overrides that of the *P*,*P*-**3** diastereomer, effectively leading to a nearly mirror-image CD spectrum at 113 K (see Fig. 4 for the X-ray determined structures of **3**).

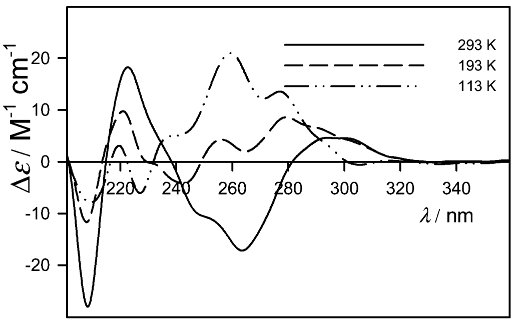

Fig. 5 Variable-temperature CD spectra of **3** in ethanol–methanol (4:1) solution.

In conclusion, we achieved the synthesis of diphenimide bis-propellers and determined by CD spectroscopy and X-ray analysis that adjacent helical propellers prefer homohelical conformations. This preference apparently originates from static interactions between component helical propellers and is likely to be further exploited in more complex molecular devices. In addition, molecular helicity correlation shows relevance for mechanical models of the compatibility of gears having like-handed helicity.

Experimental

Preparation and analytical data of diphenimides **1**–**5**, as well as computational details, are deposited as Electronic supplementary information (ESI).

X-Ray crystallography

Crystal data for **2b**: $C_{22}H_{17}NO_2$, $M = 327.37$, monoclinic, $a = 9.764(2)$, $b = 10.273(2)$, $c = 17.099(3)$ Å, $\beta = 95.55(3)^\circ$, $U = 1707.1(6)$ Å^3, $T = 295$ K, space group $P2_1/n$, $Z = 4$, μ(Mo–Kα) = 0.082 mm^{-1}, 8427 reflections measured, 2981 unique ($R_{int} = 0.016$), which were used in all calculations. The final $wR(F^2)$ was 0.115 (all data).

Crystal data for **3**: $C_{34}H_{26}N_2O_4$, $M = 526.57$, monoclinic, $a = 9.907(2)$, $b = 12.579(3)$, $c = 21.288(4)$ Å, $\beta = 98.90(3)^\circ$, $U = 2621(1)$ Å^3, $T = 295$ K, space group $P2_1$, $Z = 4$, μ(Cu-Kα = 0.707 mm^{-1}), 9356 reflections measured, 8760 unique ($R_{int} = 0.022$), which were used in all calculations. The final $wR(F^2)$ was 0.095 (all data).

Crystal data for **4**: $C_{34}H_{20}N_2O_4$, $M = 520.52$, monoclinic, $a = 9.855(2)$, $b = 12.280(2)$, $c = 20.602(4)$

Å, $\beta = 97.97(3)^\circ$, $U = 2469.2(8)$ Å^3, $T = 295$ K, space group $P2_1/n$, $Z = 4$, μ(Cu-Kα) = 0.750 mm^{-1}, 4039 reflections measured, 3920 unique ($R_{int} = 0.057$), which were used in all calculations. The final $wR(F^2)$ was 0.143 (all data).

Crystal data for **5**: $C_{29}H_{18}N_2O_4$, $M = 458.45$, monoclinic, $a = 17.325(3)$, $b = 8.587(2)$, $c = 14.868(3)$ Å, $\beta = 106.36(3)^\circ$, $U = 2122.4(8)$ Å^3, space group $C2/c$, $Z = 4$, μ(Cu-Kα) = 0.788 mm^{-1}, 1844 reflections measured, 1792 unique ($R_{int} = 0.039$), which were used in all calculations. The final $wR(F^2)$ was 0.110 (all data).

CCDC reference numbers 187215–187218. See http://www.rsc.org/suppdata/nj/b2/b207375g/ for crystallographic data files in CIF or other electronic format.

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