for [24]annulene. Planarity is apparently the most important factor for the delocalization of the π-electrons. The presence of a local aromatic nucleus like thiophene does not interfere with the paratropic behaviour of the molecule.

Experimental. *[2$_4$](2,5)Thiophenophanetetraene*, 1. 2,5-Thiophenedicarbaldehyde (5 mmol) and the bistriphenylphosphonium salt of 2,5-bis(chloromethyl)thiophene (5 mmol) were mixed in dry dimethylformamide (250 ml) in a three-necked flask equipped with a mechanical stirrer and a dropping funnel. The temperature was kept at -40 °C with a thermostat-controlled cooling bath, and oxygen-free nitrogen was slowly flushed through the system. Lithium ethoxide in ethanol (*ca.* 0.3 M) was added dropwise at a rate allowing the coloured ylid to react between successive additions. The rate of reaction was fast in the beginning but slow after *ca.* half of the required base had been added. The addition took 24 h. When no colour change was observed on addition of base, the reddish solution was warmed to room temperature, diluted with water, and extracted with ether. The ether solution was washed with water, dried, and the solvent evaporated. The residue was chromatographed on silica gel with tetrachloromethane as eluent. The first reddish fractions yielded the desired product, [2$_4$](2,5)-thiophenophanetetraene, *1* (50 mg, 4.6 %, m.p. 210–215 °C). Later fractions, according to their NMR spectra, contained complex mixtures and were not further investigated. The product was assigned as the all-*cis* isomer. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.32$ and 6.19 (8 H, s, thiophene) (8 H, s, olefin), assigned by comparison with other cyclophanes [2]. On cooling the sample to -60 °C, the two singlets separated further to $\delta = 7.57$ and 6.09. UV (C_6H_{12}): 370 nm (sh), 354 (log $\varepsilon = 4.78$) and 298 (4.46). IR (KBr): 1595 cm^{-1} (m), 1445 (m), 1402 (m), 1235 (m), 1108 (m), 842 (m) and 816, 804, 800 (sh), 795 (s). MS (70 eV): *m/e* 432 (M^+, 100 %), 399 (4.0), 398 (4.2), 366 (4.4), 365 (5.8), 364 (4.2), 333 (5.1), 332 (3.6) and 216 (M^{2+}, 9.6). Abs. mass 432.0145 ± 0.002; calc for $C_{24}H_{16}S_4$ 432.0135.

[2$_4$]Thiophenophanetetraene, dissolved in cyclohexane or benzene with traces of iodine, was photolyzed in a Rayonet reactor. Light with maximum intensity at 254 or 300 nm was used. Only a slow decomposition of the cyclophane was observed.

[2](2,5)Furano[2](2,5)thiopheno[2](2,5)furano[2](2,5)thiophenophanetetraene, 2, prepared by the above method from 2,5-furandicarbaldehyde and the bistriphenylphosphonium salt of 2,5-bis(chloromethyl)thiophene, was found to be rather unstable and difficult to purify due to rapid decomposition. ^{1}H NMR (270 MHz, $CDCl_3$) of freshly chromatographed sample: $\delta =$ 7.23 (4 H, s, thiophene protons), 6.73 (4 H, s, furan protons), 6.19 (4 H, d) and 5.92 (4 H, d, $J = 12.3$ Hz, olefinic protons).

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Preferred Conformational Angles in Peptides Unperturbed by Hydrogen Bonding and α-Substituents

JOHANNES DALE, PER GROTH and KIRSTEN TITLESTAD

Kjemisk Institutt, Universitetet i Oslo, Blindern, Oslo 3, Norway

With the recent X-ray structure determinations of cyclohexasarcosyl [1] and cyclodecasarcosyl,[2] which turned out to have the configuration sequences, *cis,cis,trans,cis,cis,trans* and *cis,cis,cis,trans,trans,cis,cis,cis,trans,trans*, respectively, some striking common features and

Table 1. Sets of torsion angles for cyclic sarcosine peptides.

	Number of possible isomers	In crystal	In $CDCl_3$ soln. at room temp.	*cis* N ϕ	*cis* CO ψ	*cis* N ϕ	*trans* CO ψ	*trans* N ϕ	*cis* CO ψ	*trans* N ϕ	*trans* CO ψ	Ref.
Sar_4	6	ctct	100 % ctct			−94	170	(−121	66)			14
Sar_5	8	cctt	>90 % cctt	−103	173	−69	172	(−123	70)	−64	148	15
				−89	176							
Sar_6	14	cctct	mixture	−75	170	−74	167	−75	138			1
Sar_7	20	ccctttt	mixture	−87	180	−72	177	(−134	69)	−87	−176	16
				−92	−164					−64	−169	
				−82	180							
Sar_8	38	cctcctt	100 % cctcctt	−107	180	−77	−167	−93	179	−71	167	17
				−92	−176	−72	−167	−83	173	−77	173	
Sar_{10}	100	ccctcccctt	–	−74	−165	−72	−174	−84	−173	−82	−178	2
				−101	−176							

regularities have become apparent for a whole series of cyclic peptides of sarcosine, excluding the lowest members (cyclodisarcosyl [3] and cyclotrisarcosyl [4]) which are constrained to an all-*cis* amide configuration and have torsion angles largely imposed by the ring structure.

These simple model substances were synthesized [5,6] in the hope of revealing the intrinsically preferred conformational angles unperturbed by the skeletal adjustments required to obtain good internal or external hydrogen bonding and by the trivial steric effects of large α-substituents. Because of the similar energy of *cis*- and *trans*-amide configurations and the observed absence of transannular interactions, the particular *cis,trans* sequence chosen by each ring among the great number of possible ones (Table 1) can be expected to be optimal. This is supported by the fact that the crystal conformation, at least as defined by the *cis,trans* sequence, is in several cases found to be alone, or dominant, also in solution.[7,8]

The table shows all thirty independently observed pairs of torsion angles, ϕ and ψ, for adjacent NC_α and $C_\alpha C$ bonds with the relative signs indicated,[9] choosing for each pair a negative sign of ϕ so as to allow easy comparison with proteins and poly-α-amino acids where the L-configuration generally favours this sign. It is seen that the values are largely concentrated in the region $\phi = 70 - 95°$ and ψ around 180°, and it makes no significant difference whether the adjoining amide groups are in *cis*- or *trans*-configuration, except possibly that the highest ϕ values are obtained when the amide on the carbonyl side is *cis*. The three exceptions form a second group with ϕ in the region $120 - 135°$ and ψ close to 70° with opposite sign, and this occurs exclusively when the amide on the carbonyl side is *cis* and on the nitrogen side *trans*.

The data of the table have been plotted in a conformational map (Fig. 1) displaced along both coordinates by 180° from the usual peptide conformational map.[9] This has the advantage of showing conformational minima grouped on both sides of ϕ or $\psi = 180°$ in a single area, torsion angles grouped on both sides of 0° being more rare. It is also more generally suitable for other compounds, for example in showing all easy interconversion paths for pentane unbroken within the map area.

The major group of torsion angle pairs for cyclosarcosyl peptides falls in the general area broadly defined [10] for protein structures as "extended chain", but is distinctly separated from the main region for hydrogen-bonded β-structures of α-substituted L-amino-acids in proteins [10] and homopolymers [9] and above all for β-structures involving glycine.[10] It is closer to the region for the non-hydrogen-bonded L-proline in proteins [10] and in helical homopolymers, both all-*cis* [11] and all-*trans*,[12] and to the metastable polyglycine helix [13] having no internal hydrogen bonds. The positions of

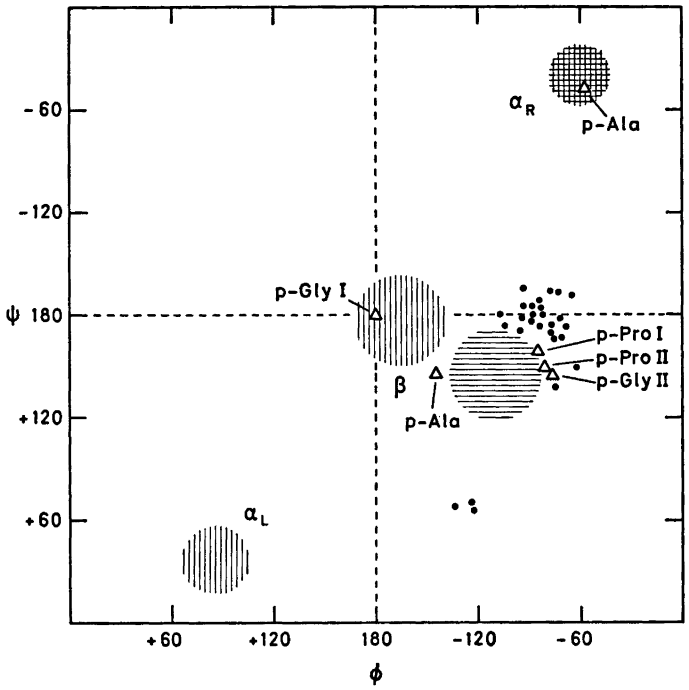

Fig. 1. Conformational map showing sets of torsion angles (sign of ϕ chosen negative) for cyclic sarcosine peptides (black dots), compared with those for poly-α-L-aminoacids (triangles), and the most common regions for glycine (vertical hatching) and α-alkyl-L-aminoacids (horizontal hatching) in proteins. Extended chain = β, righthanded α-helix = α_R, lefthanded α-helix = α_L.

various extended chains seen on this map suggest that the effect of the L-α-substituent, including the proline ring structure, is to decrease the ψ-angle from $\sim 180°$ to $+150°$; the effect of replacing *N*-methyl with NH and establishing hydrogen bonds is to increase the ϕ angle from about $-80°$ to near 180°; and the combined effect of both is to give the same decrease of ψ but intermediate increase of ϕ.

The minor group of torsion angle pairs for cyclosarcosyl peptides is completely isolated in the map. Since this combination occurs only in the smaller of the rings, it must be of lower stability and used only when the ring structure requires the sharp bend possible by the sequence $\omega = 0$ (*cis*), $\psi \sim 70°$. However, if the ϕ value were then to remain near $-80°$ the bend would be too sharp, and the transannular repulsion widens the ϕ angle to $\sim -130°$. It is also easy to see that for simple steric reasons the sequence $\omega = 0$, $\psi = 60°$, $\phi = 120°$, $\omega' = 0$ is impossible (except in a cyclic tripeptide) and thus explains why the amide configuration on the nitrogen side must be *trans* ($\omega' = 180°$).

It thus looks as if there is a substantial ethane-like intrinsic barrier in the $C_\alpha - C$ bond and that the ψ-angle is preferentially *anti*, the alternative *gauche* being found only in the smaller rings. The total spread of ϕ angles over a single wider range ($64 - 134°$) suggests the absence of an intrinsic barrier in the $N - C_\alpha$ bond, and a simple steric repulsive balance between the carbonyl oxygen and the two substituents on the nitrogen of the same residue (methyl and the main chain).

The general occurrence of sequences of only *cis*- or only *trans*-amide configuration in the larger rings (Table 1) is difficult to understand. It is striking, however that in these crystal conformations the carbonyl oxygen of all *cis*-amide groups tend to point out of the ring whereas oxygen of *trans*-amide groups point into the ring, orienting themselves against the positive end of *cis*-amide groups across the ring. Similar and well-known examples of induction of identical configuration are shown by poly-L-proline, which crystallizes as all-*trans* from polar solvents and as all-*cis* from less polar solvents. It may be significant that in the all-*trans* helix [12] the carbonyl oxygens point outwards (to the polar solvent) whereas in the all-*cis* helix [11] each oxygen is oriented towards the positive end of other amide groups further along the axis.

The synthesis of cyclodecasarcosyl has not been reported before. The *N*-protected decapeptide was obtained by coupling two pentapeptides, using the same general methods as already described,[6] and the trichlorophenyl ester cyclized in pyridine, yield 50 %, m.p. 280 – 282 °C.

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On the Fluorescence of Propellicene

EDVARD M. KOSOWER [a,b], HANNA DODIUK,[a] BENGT THULIN [c] and OLOF WENNERSTRÖM [c]

[a] Department of Chemistry, Tel-Aviv University, Ramat-Aviv, Tel-Aviv, Israel, [b] Department of Chemistry, State University of New York, Stony Brook, USA 11794 and [c] Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, Fack, S-402 20 Göteborg, Sweden

Certain crowded polyaromatic molecules, most notably 9,9′-bianthracene,[1,2] exhibit a surprising charge-transfer emission in many solvents. Although the theory of the emission has not been worked out in detail, the observation of a charge-transfer emission may be ascribed to (a) fluctuations in the solvent arrangements within a sufficiently polar solvent environment which permit the evolution of a cybotactic region [3] that stabilizes a charge-transfer state and (b) lack of rapid quenching pathways for nonradiative decay of the charge-transfer state. In 9,9′-bianthracene, a perpendicular relationship of the two rings leads to decay rates of the charge-transfer state which are lower than the radiative rate.[4] It was thus of interest to find whether the unusual cyclic helicene, propellicene (see Fig. 1; the formula),[5] could give rise to charge-transfer emissions.

Fluorescence spectra were measured in dioxane and dioxane-water mixtures, and in glycerol. The insolubility of propellicene in glycerol forced us to examine a dispersion of a dioxane solution of the compound in glycerol. The fluorescence lifetimes and quantum yields of fluorescence were also measured in dioxane and 33 % dioxane-water solutions.

In no case was a charge-transfer emission observed. The fluorescence quantum yield is not particularly high, but the quenching mechanisms were not further investigated. A structured fluorescence spectrum with peaks at 413 and 433 nm (shoulders at 463 and 495 nm) can be observed in dioxane. Addition of water does not affect the emission spectrum until a composition of 33 % dioxane-water is reached, at which point, the spectrum shifts to 10 nm longer wavelengths without change in excitation spectrum. The excitation spectrum in all cases was identical with the absorption spectrum.

Lifetime data and derived rate constants are shown in Table 1. The fluorescence lifetimes of helicenes are extremely long [6] and propellicene is no exception. The absorption and fluorescence spectra of propellicene resemble those of hexahelicene.[6]

The change in position of the fluorescence maxima in 33 % dioxane-water from those found for pure dioxane is probably due to an aggregate (dimer?) of propellicene. The spec-