cells of $C_{24}H_{50}$ and $C_{26}H_{54}$ with the unit cells for the shorter even alkanes ($C_{18}H_{38}$, $C_{20}H_{42}$ and $C_{22}H_{46}$) and the observation of α and β being near 90° suggests a polytypic structure containing two layers of triclinic ($Z = 1$) 'type' unit cells related by a pseudo-twofold axis nearly perpendicular to the (00l) plane. This analysis is also substantiated by the similarity of γ for $C_{24}H_{50}$ and $C_{26}H_{54}$ to the value (180 − γ) for the shorter even n-alkanes.

These results emphasize the necessity of obtaining good-quality powder diffraction data over a wide range of 2θ in order to reliably identify such low-symmetry phases. Much of the confusion in the literature surrounding identification of alkane phases results either from impure samples or poor-quality data. High-resolution powder diffraction using a synchrotron source now provides an available technique capable of resolving the phase structure of the n-alkanes and other related low-symmetry materials.

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Conformational Analysis of Rotational Barriers in *N*-Arylpyrrolidin-2-ones

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Abstract

The structures of *N*-phenylpyrrolidin-2-one and the three isomeric *N*-tolylpyrrolidin-2-ones have been studied by single-crystal X-ray diffraction, as a basis for the conformational analysis of the barrier to rotation around the single bond between the rings. Force-field simulation of the molecular structure is consistent with a rotational barrier of 7 kJ mol⁻¹. Crystal data: *N*-phenylpyrrolidin-2-one, orthorhombic, *Pbca*, $a = 14.114\,(3)$, $b = 6.879\,(4)$, $c = 17.386\,(5)$ Å, $R = 0.059$ for 1110 unique reflections [$F_o \geq 4\sigma(F_o)$]; *N*-(2-methylphenyl)pyrrolidin-2-one, orthorhombic, *Pbca*, $a = 16.999\,(4)$, $b = 16.411\,(2)$, $c = 7.008\,(2)$ Å, $R = 0.077$ for 1479 unique reflections [$F_o \geq 4\sigma(F_o)$]; *N*-(3-methylphenyl)pyrrolidin-2-one, monoclinic, $P2_1/c$, $a = 10.411\,(2)$, $b = 7.645\,(2)$, $c = 12.782\,(1)$ Å, $\beta = 110.32\,(1)°$, $R = 0.065$ for 1641 unique reflections [$F_o \geq 4\sigma(F_o)$]; *N*-(4-methylphenyl)pyrrolidin-2-one, orthorhombic, $P2_12_12_1$, $a = 7.668\,(2)$, $b = 10.804\,(2)$, $c = 11.456\,(1)$ Å, $R = 0.054$ for 1155 unique reflections [$F_o \geq 4\sigma(F_o)$].

Introduction

Elementary theory predicts that bonds of even order produce sterically rigid structures whereas those of

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odd order are cylindrically symmetrical and thus allow free rotation. Where a measurable barrier to rotation occurs, associated with a single bond, it is therefore often ascribed to non-integral bond orders arising from electronic factors, the most obvious of which is resonance. In molecules such as N-aryl-pyrrolidin-2-ones (I), restricted rotation around the central bond could hence arise from resonance involving the carbonyl group, the nitrogen lone pair and the aromatic system (see below). Under this scheme the occurrence of the barrier should be accompanied by shorter N—C(Ar) and N—C(O) bonds, a longer C—O distance and a planar system.

(II)	R=H
(III)	R=o-Me
(IV)	R=m-Me
(V)	R=p-Me

(I)
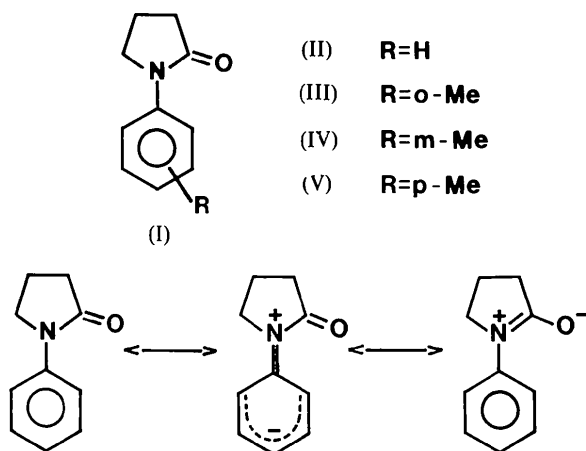
Different R substituents on the aromatic ring should have a recognizable effect, if not on the bond lengths, then certainly on the dihedral angle between the two molecular fragments. To test these ideas experimentally, a series of compounds with different R has been studied crystallographically as reported below. Molecular mechanics was used to distinguish between steric and electronic factors.

The only other reports of related structures were by Baker, King & McOmie (1981) who characterized a by-product, 5-cyano-1,4,5-triphenylpyrrolidin-2-one, crystallographically, and by Fujiwara, Varley & Van der Veen (1977), who examined the o-bromo derivative of (I).

Experimental

Routine measurements were carried out using a Kofler micro hot-stage (m.p.), and Cary 2300 (UV) and Bruker AC200 (NMR) spectrometers. ^{1}H spectra were recorded at 200·13 MHz, and ^{13}C spectra at 50·32 MHz. Column chromatography was carried out using Merck silica gel (particle size 0·063–0·200 mm).

N-Arylpyrrolidin-2-ones were prepared by slight modification of a reported procedure (Reppe, 1955).

A mixture of the appropriate aniline (0·1 mol) and γ-butyrolactone (0·11 mol) was heated at 473–503 K for *ca* 4 h. The resulting viscous liquid was cooled; concentrated sulfuric acid (1 ml) was added, and heating was resumed for a further *ca* 2 h. The crude product was cooled and partitioned between chloroform (50–100 ml) and aqueous hydrochloric acid (2M, 100 ml). The organic phase was washed with saturated aqueous sodium hydrogen carbonate and sodium chloride solutions (100 ml of each), dried (MgSO₄), and evaporated *in vacuo*. The crude product thus obtained was purified further by recrystallization, preceded by column chromatography on silica gel if necessary. Yields were in the range 50–70%.

N-Phenylpyrrolidin-2-one: m.p. 341 K [from hexane–ethyl acetate; lit. m.p. (Reppe, 1955) 340–341 K]; λ_{max} 246 and 279 (shoulder) nm (ε_{max} 12600 and 820); δ_H (CDCl₃) 7·61 (2H, br. d, J *ca* 8·5 Hz, arom. 2-H and 6-H), 7·34 (2H, br. t, J 7·0 Hz, arom. 3-H and 5-H), 7·11 (1H, m, arom. 4-H), 3·80 (2H, t, J 7·0 Hz, 5-H), 2·56 (2H, t, J 8·1 Hz, 3-H), 2·10 (2H, quintet with fine coupling, J *ca* 7·7 Hz, 4-H); δ_C (CDCl₃) 173·9 (C=O), 139·2 (arom. C-1), 128·5, 124·1 (arom. C-4), 119·6, 48·5 (C-5), 32·5 (C-3), 17·7 (C-4).

N-(2-Methylphenyl)pyrrolidin-2-one: m.p. 319–321 K [from diisopropyl ether–hexane; lit. m.p. (Reppe, 1955) 320 K]; λ_{max} 265 and 270 nm (ε_{max} 1815 and 1835); δ_H (CDCl₃) 7·27–7·10 (4H, br. m, arom. H), 3·70 (2H, t, J 7·0 Hz, 5-H), 2·56 (2H, t, J 8·0 Hz, 3-H), 2·23 and 2·20 (5H, s and m, J *ca* 7·7 Hz, CH₃ and 4-H); δ_C (CDCl₃) 174·1, 137·3, 135·3, 130·9, 127·6, 126·6, 126·4, 50·5 (C-5), 31·0 (C-3), 18·9 (C-4), 17·7 (CH₃).

N-(3-Methylphenyl)pyrrolidin-2-one: m.p. 330 K [from cyclohexane–pentane; lit. m.p. (Reppe, 1955) 331 K]; λ_{max} 248 and 283 (shoulder) nm (ε_{max} 12050 and 1600); δ_H (CDCl₃) 7·43 (1H, br. t, J 0·5 Hz, arom. 2-H), 7·36 (1H, br. dt, J 7·8 and 0·5 Hz, arom. 4-H), 7·16 (1H, t, J 7·8 Hz, arom. 5-H), 6·92 (1H, d, J 7·5 Hz, arom. 6-H), 3·74 (2H, t, J 7·0 Hz, 5-H), 2·51 (2H, t, J 7·2 Hz, 3-H), 2·33 (3H, s, CH₃), 2·04 (2H, quintet with fine coupling, J *ca* 7·3 Hz, 4-H); δ_C (CDCl₃) 173·7 (C=O), 139·0, 138·0, 128·1, 124·7, 120·2, 116·5, 48·4 (C-5), 32·3 (C-3), 21·2 (CH₃), 17·5 (C-4).

N-(4-Methylphenyl)pyrrolidin-2-one: m.p. 360–361 K [from ethyl acetate; lit. m.p. (Braunholtz & Mann, 1957), 360·5 K]; λ_{max} 249 and 285 (shoulder) nm (ε_{max} 13600 and 820); δ_H (CDCl₃) 7·39 (2H, d, J 8·6 Hz), 7·07 (2H, d, J 8·6 Hz), 3·77 (2H, t, J 7·0 Hz, 5-H), 2·50 (2H, t, J 8·0 Hz, 3-H), 2·24 (3H, s, CH₃), 2·01 (2H, quintet with fine coupling, J *ca* 7·5 Hz, 4-H); δ_C (CDCl₃) 174·0 (C=O), 136·8, 134·0, 129·2, 119·9, 48·8 (C-5), 32·5 (C-3), 20·7 (CH₃), 17·9 (C-4).

Table 1. *Crystal data and details of the crystallographic analyses*

	(II)	(III)	(IV)	(V)
Formula	$C_{10}H_{11}NO$	$C_{11}H_{13}NO$	$C_{11}H_{13}NO$	$C_{11}H_{13}NO$
M_r	161·20	175·23	175·23	175·23
Space group	*Pbca*	*Pbca*	$P2_1/c$	$P2_12_12_1$
a (Å)	14·114 (3)	16·999 (4)	10·411 (2)	7·668 (2)
b (Å)	6·879 (4)	16·411 (2)	7·645 (2)	10·804 (2)
c (Å)	17·386 (5)	7·008 (2)	12·782 (1)	11·456 (1)
β (°)			110·32 (1)	
V (Å³)	1687·93	1954·90	954·05	949·02
D_x (g cm⁻³)	1·27	1·19	1·22	1·23
$F(000)$	688	752	376	376
Z	8	8	4	4
μ(Mo $K\alpha$) (cm⁻¹)	0·47	0·43	0·44	0·44
Scan	ω–2θ	ω–2θ	ω–θ	ω–2θ
Vertical aperture (mm)	4	4	4	4
Horizontal aperture (mm)	1·5	1·8	1·8	2·7
Scan speed (° min⁻¹)	< 5·49	< 5·49	< 5·49	< 5·49
Range (°)	$2 \le \theta \le 30$	$3 \le \theta \le 30$	$2 \le \theta \le 30$	$2 \le \theta \le 30$
h	0–19	0–23	0–14	– 10–10
k	0–9	0–23	0–10	0–15
l	0–24	0–9	–18–18	0–16
Reflections	2822	3897	3113	3030
No. of unique $F_o \ge 4\sigma(F_o)$	1110	1479	1641	1155
Parameters	110	122	122	122
Maximum (shift/e.s.d.)	0·01	0·06	0·33	0·29
R	0·059	0·077	0·065	0·054
wR [$w \propto 1/\sigma^2(F)$]	0·054	0·076	0·061	0·047
Residual density (e Å⁻³)				
Maximum	0·20	0·31	0·21	0·30
Minimum	– 0·25	– 0·33	– 0·19	– 0·35

Structure determination

Crystals of (II), (III), (IV) and (V) were examined by standard single-crystal methods using a CAD-4 diffractometer at room temperature. Cell constants were obtained from least-squares refinement of 25 high-angle θ values. All structures were solved by routine use of the *SHELX* set of programs (Sheldrick, 1985). Crystal data and details of the analysis are given in Table 1. Data reduction consisted of corrections for background, Lp and absorption by the empirical method of North, Phillips & Mathews (1968). Refined atomic coordinates are collated in Table 2.*

Relevant molecular parameters are collected in Table 3, and were used as a basis for the conformational analysis by molecular mechanics. Atomic numbering schemes are defined on the stereoscopic molecular drawings in Fig. 1.

Conformational analysis

For none of the four compounds examined here was the molecular geometry in the region around the central bond found to be consistent with delocalization according to the scheme considered before. N—C(1) is consistently shorter than N—C(4), showing double-bond character. On the other hand,

Table 2. *Refined fractional atomic coordinates* ($\times 10^4$) *with estimated standard deviations and equivalent isotropic thermal parameters* (Å² $\times 10^3$) *of non-*H *atoms, or common isotropic temperature factors for* H *atoms*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Compound (II)				
N	1257 (2)	711 (3)	4044 (1)	45 (1)
O	1406 (2)	– 1882 (3)	4861 (1)	67 (1)
C(1)	1342 (2)	– 142 (5)	4745 (2)	48 (1)
C(2)	1377 (2)	1421 (5)	5358 (2)	56 (1)
C(3)	1035 (3)	3214 (5)	4938 (2)	63 (1)
C(4)	1282 (3)	2860 (4)	4098 (2)	55 (1)
C(5)	1273 (2)	– 210 (4)	3323 (2)	42 (1)
C(6)	882 (2)	– 2069 (4)	3230 (2)	51 (1)
C(7)	864 (2)	– 2903 (5)	2511 (2)	62 (1)
C(8)	1222 (2)	– 1945 (6)	1877 (2)	67 (1)
C(9)	1617 (3)	– 122 (5)	1982 (2)	64 (1)
C(10)	1643 (2)	728 (5)	2696 (2)	55 (1)
H(21)	2091 (2)	1621 (5)	5567 (2)	84 (3)
H(22)	916 (2)	1071 (5)	5835 (2)	84 (3)
H(31)	280 (3)	3385 (5)	5011 (2)	84 (3)
H(32)	1393 (3)	4497 (5)	5148 (2)	84 (3)
H(41)	1975 (3)	3423 (4)	3958 (2)	84 (3)
H(42)	760 (3)	3510 (4)	3723 (2)	84 (3)
H(6)	597 (2)	2852 (4)	3716 (2)	84 (3)
H(7)	556 (2)	– 4329 (5)	2439 (2)	84 (3)
H(8)	1204 (2)	– 2618 (6)	1316 (2)	84 (3)
H(9)	1905 (3)	646 (5)	1493 (2)	84 (3)
H(10)	1955 (2)	2152 (5)	2763 (2)	84 (3)
Compound (III)				
O	4563 (1)	1668 (1)	– 1437 (3)	69 (1)
N	3727 (1)	1351 (1)	1015 (3)	43 (1)
C(1)	4441 (2)	1526 (2)	253 (4)	49 (1)
C(2)	5042 (2)	1541 (2)	1827 (5)	63 (1)
C(3)	4621 (2)	1142 (2)	3508 (5)	70 (1)
C(4)	3759 (2)	1316 (2)	3117 (4)	57 (1)
C(5)	2998 (1)	1360 (2)	19 (3)	40 (1)
C(6)	2861 (2)	823 (2)	– 1490 (4)	48 (1)
C(7)	122 (2)	854 (2)	– 2358 (4)	62 (1)
C(8)	1535 (2)	1372 (2)	– 1740 (5)	66 (1)
C(9)	1683 (2)	1891 (2)	– 228 (4)	59 (1)
C(10)	2411 (2)	1888 (2)	631 (4)	49 (1)
C(11)	3471 (2)	215 (2)	– 2155 (4)	65 (1)
H(21)	5557 (2)	1195 (2)	1428 (5)	95 (3)
H(22)	5212 (2)	2158 (2)	2166 (5)	95 (3)
H(31)	4805 (2)	1412 (2)	4841 (5)	95 (3)
H(32)	4731 (2)	494 (2)	3544 (5)	95 (3)
H(41)	3583 (2)	1889 (2)	3740 (4)	95 (3)
H(42)	3389 (2)	834 (2)	3661 (4)	95 (3)
H(7)	2009 (2)	464 (2)	– 3568 (4)	95 (3)
H(8)	965 (2)	1363 (2)	– 2418 (5)	95 (3)
H(9)	1231 (2)	2303 (2)	264 (4)	95 (3)
H(10)	2526 (2)	2298 (2)	1801 (4)	95 (3)
H(111)	3755 (2)	– 15 (2)	– 885 (4)	95 (3)
H(112)	3899 (2)	525 (2)	– 3034 (4)	95 (3)
H(113)	3219 (2)	– 287 (2)	– 2945 (4)	95 (3)
Compound (IV)				
O	6333 (2)	1593 (3)	4236 (1)	83 (1)
N	5026 (2)	1213 (3)	2382 (2)	43 (1)
C(1)	6229 (3)	1421 (3)	3264 (2)	50 (1)
C(2)	7395 (3)	1459 (4)	2830 (2)	54 (1)
C(3)	6779 (3)	868 (4)	1616 (2)	56 (1)
C(4)	5238 (3)	1171 (4)	1306 (2)	52 (1)
C(5)	3693 (2)	1253 (3)	2441 (2)	42 (1)
C(6)	2588 (3)	1701 (3)	1492 (2)	48 (1)
C(7)	1265 (3)	1739 (4)	1509 (2)	56 (1)
C(8)	1047 (3)	1306 (4)	2482 (2)	66 (1)
C(9)	2140 (3)	839 (4)	3421 (2)	63 (1)
C(10)	3465 (2)	804 (3)	3421 (2)	50 (1)
C(11)	87 (3)	2293 (4)	483 (3)	80 (1)
H(21)	7801 (3)	2768 (4)	2875 (2)	102 (3)
H(22)	8200 (3)	580 (4)	3302 (2)	102 (3)
H(31)	7181 (3)	1633 (4)	1089 (2)	102 (3)
H(32)	6990 (3)	– 500 (4)	1541 (2)	102 (3)
H(41)	4660 (3)	120 (4)	790 (2)	102 (3)
H(42)	4940 (3)	2399 (4)	871 (2)	102 (3)
H(6)	2768 (3)	2031 (3)	733 (2)	102 (3)
H(8)	23 (3)	1335 (4)	2512 (3)	102 (3)
H(9)	1950 (3)	487 (4)	4173 (2)	102 (3)
H(10)	4307 (3)	431 (3)	4159 (2)	102 (3)
H(111)	– 886 (3)	1973 (4)	561 (3)	102 (3)

Table 2 (cont.)

	x	y	z	U_{eq}
H(112)	182 (3)	1617 (4)	-229 (3)	102 (3)
H(113)	144 (3)	3687 (4)	369 (3)	102 (3)
Compound (V)				
N	1309 (3)	7596 (2)	-67 (2)	50 (1)
O	745 (3)	5543 (2)	-442 (2)	85 (1)
C(1)	1010 (3)	6603 (3)	-773 (3)	55 (1)
C(2)	1024 (3)	7021 (3)	-2019 (2)	63 (1)
C(3)	1675 (4)	8345 (3)	-1976 (3)	69 (1)
C(4)	1381 (3)	8759 (3)	-713 (3)	63 (1)
C(5)	1318 (3)	7575 (3)	1170 (2)	47 (1)
C(6)	858 (3)	8622 (3)	1790 (3)	55 (1)
C(7)	884 (4)	8623 (3)	2996 (3)	65 (1)
C(8)	1354 (3)	7580 (3)	3615 (2)	61 (1)
C(9)	1830 (3)	6528 (3)	2979 (3)	53 (1)
C(10)	1800 (3)	6518 (3)	1781 (2)	49 (1)
C(11)	1403 (4)	7586 (4)	4941 (3)	83 (1)
H(21)	1899 (3)	6455 (3)	-2530 (3)	103 (3)
H(22)	-270 (3)	6978 (3)	-2389 (2)	103 (3)
H(31)	3029 (3)	8395 (3)	-2250 (3)	103 (3)
H(32)	929 (4)	8920 (3)	-2564 (3)	103 (3)
H(41)	171 (3)	9262 (3)	-623 (3)	103 (3)
H(42)	2448 (3)	9329 (3)	-414 (3)	103 (3)
H(61)	495 (3)	9453 (3)	1326 (3)	103 (3)
H(71)	523 (4)	9451 (3)	3467 (3)	103 (3)
H(91)	2236 (3)	5707 (3)	3441 (3)	103 (3)
H(101)	2155 (3)	5690 (3)	1311 (2)	103 (3)
H(111)	1420 (4)	6623 (4)	5193 (3)	103 (3)
H(112)	296 (4)	8039 (4)	5339 (3)	103 (3)
H(113)	2591 (4)	8027 (4)	5229 (3)	103 (3)

O—C(1) is a typical double bond, N—C(5) is single, and all of the molecules are distinctly non-planar. The average non-planarity as measured by the dihedral angle is about 30°, except for the o-methyl derivative where the angle is 60°. This larger angle is almost certainly due to steric interaction, whereas an explanation only in terms of electronic effects should be found for the 30° angle observed elsewhere.

The importance of the resonance interaction between an N-aryl substituent and the lactam ring of certain β- and γ-lactams in solution has previously been inferred from the intensity of the ultraviolet chromophore at ca 250 nm (Fujiwara et al., 1977). In the present work, the unsubstituted lactam (II) and the m- and p-methyl derivatives (IV) and (V) were found to possess this chromophore, and extinction coefficients were in the range 12000–13600. By contrast, the o-methyl derivative (III) had only weak multiple bands at 265 and 270 nm, and the extinction coefficient was substantially diminished to ca 1800. The UV evidence thus convincingly indicates the relative insignificance of resonance effects between the rings in (III), and implies that the large dihedral angle observed for (III) in the solid state persists in solution.

In the case of substituted N,N'-bipyrrolidinones (Michael, Billing, Boeyens, Carlton, Denner & Hindmarch, 1990) coplanarity was found to be avoided because of lone-pair–lone-pair repulsion. Since the present situation, however, is different, detailed conformational analysis by molecular mechanics was needed to decide whether an orienting interaction towards coplanarity is operational.

The unadjusted force field in the program of Boyd (1968) did not reproduce any of the distinctive features of the observed structures, in molecular-mechanics simulation. Successful modelling was achieved by the introduction of the special force-field parameters shown in Table 4. Of particular interest is
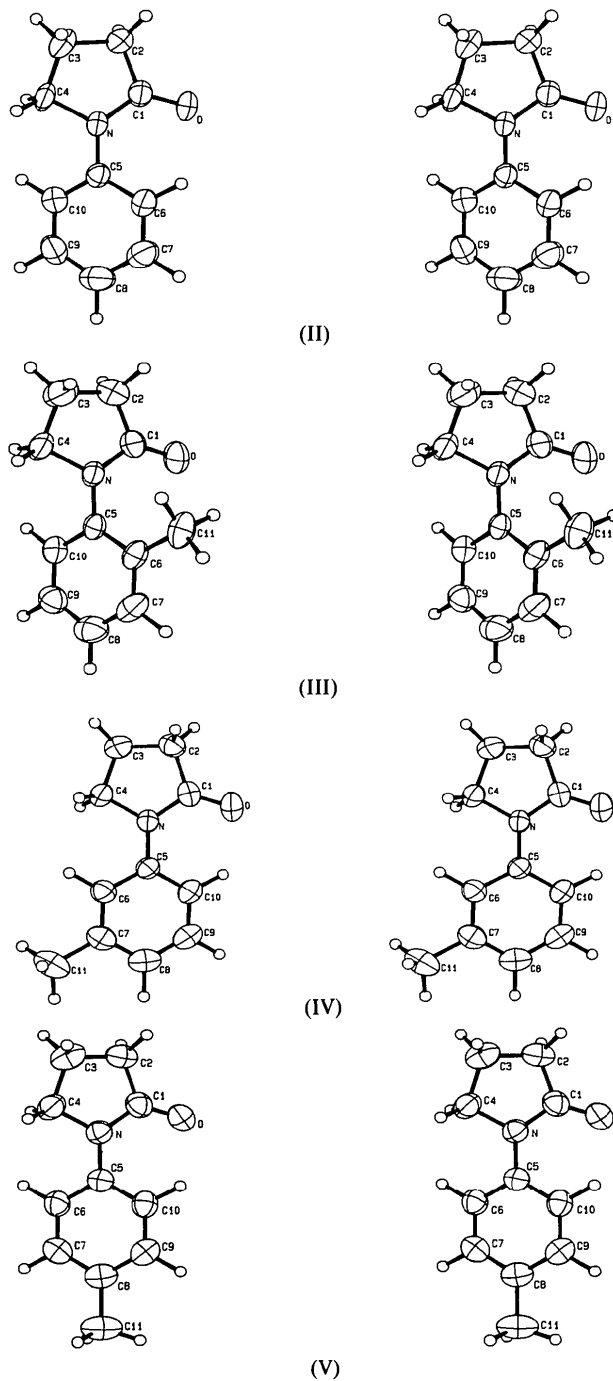

(II)

(III)

(IV)

(V)

Fig. 1. Stereoscopic drawings of the molecular conformations and atomic numbering schemes of (II), (III), (IV) and (V).

Table 3. *Important molecular parameters* (Å, °) *that define the molecular conformation* (*X-ray*) *compared with the values obtained by molecular-mechanics simulation* (*MM*)

	(II)		(III)		(IV)		(V)	
	X-ray	MM	X-ray	MM	X-ray	MM	X-ray	MM
N—C(1)	1·357 (3)	1·353	1·356 (3)	1·351	1·373 (3)	1·356	1·363 (3)	1·353
N—C(4)	1·482 (3)	1·481	1·475 (3)	1·477	1·468 (3)	1·485	1·458 (3)	1·481
N—C(5)	1·404 (4)	1·407	1·423 (3)	1·403	1·415 (3)	1·409	1·418 (3)	1·407
O—C(1)	1·218 (3)	1·221	1·225 (3)	1·221	1·217 (3)	1·221	1·224 (3)	1·221
C(1)—N—C(5)—C(6)	34·9 (2)	27·0	63·3 (2)	53·7	155·2 (3)	153·3	−151·0 (2)	−153·6
C(1)—N—C(5)—C(10)	−147·4 (4)	−153·5	−119·6 (3)	−126·4	−26·6 (1)	−27·0	31·0 (1)	26·8

Table 4. *Special bond-stretching* [*k* (mdyne Å⁻¹), *r_o* (Å)] *and angle-bending* [*k* (mdyne Å rad⁻¹), *θ_o* (rad)] *force-field parameters*

The parameters have been optimized, in combination with the standard parameters of Boyd (1968), to match the experimental structure of (II) and used to simulate the structures of (III), (IV) and (V), assuming a torsional attraction of 0·29 kJ mol⁻¹ deg⁻¹ towards the planar configuration of the phenyl rings. This corresponds to an estimated rotational barrier of 7 kJ mol⁻¹.

	k	r_o or θ_o
C(1)—C(2)	4·17	1·51
C(2)—C(3)	4·40	1·52
C(3)—C(4)	4·40	1·53
N—C(1)	8·33	1·34
N—C(4)	3·61	1·46
N—C(5)	7·50	1·39
N—C(1)—C(2)	0·41	2·094
N—C(1)—O	0·42	2·094
C(1)—N—C(5)	0·42	2·094
C(4)—N—C(5)	0·42	2·094
C(1)—N—C(4)	0·82	2·094
N—C—C	1·00	1·911

the torsional parameter of 7 kJ mol⁻¹ at the central bond, favouring the planar configuration. Without this interaction the simulation converges to the fully staggered form. The comparison between some crucial bond parameters from crystallographic analyses and from the force-field simulation is shown in Table 3. The agreement is satisfactory.

Not surprisingly, efforts to observe the low barrier to rotation of the rings by NMR spectroscopy were inconclusive. From the crystallographic results and the force-field simulation, however, the existence of the barrier is beyond dispute. Whether to interpret this result in terms of delocalization or nuclear screening (Boeyens, 1982) is not important. The distinguishing structural features would in either case be small, in view of the low barrier. The characteristic shortening of the N—C(1) bond, however, finds an easy explanation only in terms of nuclear screening by the N lone pair and C—$p\pi$ electron densities.

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Crystal and Molecular Structures of Overcrowded Halogenated Compounds. IX.* Stereochemistry of Molecules Containing the Perchlorofluorenyl and Perchlorofluorenylidene Moieties and of Their Hydrogen Analogues

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Abstract

The structures of the overcrowded perchlorofluorenyl moiety, on its own and in two poly-chlorinated bifluorenyls, are compared among themselves and with those of the parent aromatic hydrocarbons; the comparison is extended to the perchlorofluorenylidene moiety in perchlorobifluorenylidene and the fluorenylidene moieties in

* Part VIII: Herbstein (1979).