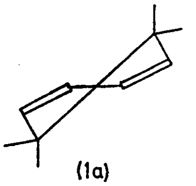
Conformational Analysis of Substituted 1,2-Dihydronaphthalenes

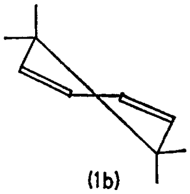
By **M. J. Cook** * and **N. L. Dassanayake**, School of Chemical Sciences, University of East Anglia, Norwich

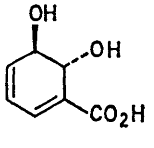
From coupling-constant data for a series of 2-substituted 1,2-dihydronaphthalenes it is concluded that 2-carboxy, 2-methoxycarbonyl, and 2-ethoxycarbonyl substituents preferentially occupy the pseudo-equatorial position whereas a 2-chlorocarbonyl group shows no conformational preference. The pseudo-axial preferences found here and elsewhere for substituents in the 1-position are discussed in terms of *peri* H interactions.

THE equatorial preferences observed for bulky substituents in cyclohexane rings are less pronounced in compounds such as 3-alkyl cyclohexanones [1] and 4-halogenocyclohexenes,[2] and this is associated at least in part with the absence of one of the normal 1,3-diaxial substituent:H interactions. The 1,3-cyclohexadiene ring system, which interconverts rapidly [3] between the non-planar forms [4-7] (Ia) and (Ib), provides an example of an analogous situation wherein a substituent group occupying one of the two pseudo-axial positions experiences no 1,3-diaxial interaction with hydrogen atoms.

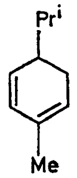
Batterham and Young [8] examined the *trans*-diol (2) and two of its derivatives but the equilibria are dominated by H-bonding and solvation effects which preclude discussion of the steric interactions involved. Earlier, o.r.d. and c.d. studies [9-11] on (−)-α-phellandrane (3) led to the conclusion that the isopropyl group is preferentially pseudo-equatorial but the equilibrium constant could not be determined [although recently, Baldwin and Krueger [12] from product analysis of the photochemical electrocyclic valence isomerisation of (3), have suggested that the equatorial isopropyl conformer is favoured by 0·42 kcal/mol]. In the solid state, an *X*-ray analysis of gliotoxin showed [13] that the cyclohexadiene ring in the molecule is fused *via* a pseudo-equatorial bond, whilst n.m.r. and c.d. studies of various benzo-fused compounds have revealed that 9-substituents on the 9,10-dihydrophenanthrene [14] system and 1-aryl substituents in some highly substituted 1,2-dihydronaphthalenes are predominantly pseudo-axial.[15-17] In a recent paper from this laboratory [18] on the conformational equilibria of the 1,4-disubstituted 1,2-dihydronaphthalenes (4a) and (4b),


(Ia)


(Ib)



(2)



(3)

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[5] G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, 1967—1968, **1**, 11.

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[15] A. F. A. Wallis, *Tetrahedron Letters*, 1968, 5287.

[16] D. C. Ayres, *Canad. J. Chem.*, 1969, **47**, 2075; D. C. Ayres and J. A. Harris, *Chem. Comm.*, 1969, 135.

[17] D. C. Ayres, J. A. Harris, and P. B. Hulbert, *J. Chem. Soc.* (*C*), 1971, 1111.

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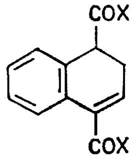
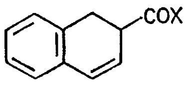
it was reported that the 1-carboxy- and 1-methoxycarbonyl groups are 90 and 75% pseudo-axial respectively.

Whilst the pseudo-axial preferences for benzylic substituents in the benzo-fused ring compounds can be attributed to the absence of 1,3-diaxial interactions, destabilisation of the pseudo-equatorial position by the neighbouring aryl proton * may well be the overriding factor. In an attempt to assess the relative importance of these two factors we have now investigated, by means of coupling-constant data, the conformational equilibria of 1,2-dihydronaphthalene-2-carboxylic acid (5a) and its derivatives (5b—d), and we compare the results with data for (4a), (4b),[18] and the corresponding acid chloride (4c). The effect of a 4-substituent group on the conformation of the 1,2-dihydronaphthalene ring system is also considered.



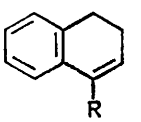
(4)

a; X = OH
b; X = OMe
c; X = Cl



(5)

a; X = OH
b; X = OMe
c; X = OEt
d; X = Cl



(6)

a; R = CO_2H
b; R = H

Preparation of Compounds.—The bis(acid chloride) (4c) was prepared from the bisacid [19] (4a) using thionyl chloride in ether. The crude product decomposed to 1-naphthoyl chloride during distillation (*cf.* the ready decomposition of 1,2-dihydrophthaloyl chloride [20]) and was therefore characterised by spectroscopy. The n.m.r. spectrum showed that the product was free from starting material and side-products.† Literature routes or standard interconversions were used for the preparation of 1,2-dihydronaphthalene-2-carboxylic acid and its derivatives (5b), (5c), and (5d), and for 1,2-dihydronaphthalene-4-carboxylic acid (6a).

EXPERIMENTAL

I.r. spectra were obtained of liquid films or Nujol mulls on a Perkin-Elmer 257 spectrophotometer. N.m.r. spectra were obtained on Varian HA-100 and Jeol-C-60H spectrometer systems; the 100 MHz spectra at 38°, the 60 MHz spectra at 27°.

Compounds.—The following were obtained by literature methods: 1,2-dihydronaphthalene-2-carboxylic acid,[23] m.p. 100° (lit.,[24] m.p. 100—101°); methyl 1,2-dihydronaphthalene-2-carboxylate, b.p. 100°/0·35 mm (lit.,[25] b.p. 143—144°/9 mm); ethyl 1,2-dihydronaphthalene-2-carboxylate, b.p. 85°/0·05 mm (lit.,[26] b.p. 152—153°/12 mm); 1,2-dihydronaphthalene-4-carboxylic acid, m.p. 115° (lit.,[24] m.p. 120°).

1,2-*Dihydronaphthalene*-2-*carbonyl Chloride.*—1,2-Dihydronaphthalene-2-carboxylic acid (0·20 g) and thionyl chloride (15 ml) in ether (10 ml) were maintained at 30—40° for 6 h. Ether and excess of thionyl chloride were removed by evaporation under reduced pressure and the residual oil was distilled. 1,2-*Dihydronaphthalene*-2-*carbonyl chloride* (0·15 g, 75%) was collected at 65°/0·08 mm (Found: C, 68·3; H, 5·2. $C_{11}H_9OCl$ requires C, 68·6; H, 4·7%), $\nu_{max.}$ 1790 cm^{-1}.

1,2-*Dihydronaphthalene*-1,4-*dicarbonyl Dichloride.*—1,2-Dihydronaphthalene 1,4-dicarboxylic acid [19] (0·59 g) and thionyl chloride (15 ml) in ether were maintained at 30—40° for 4 h and at room temperature for 48 h. The solvent and excess of thionyl chloride were removed by evaporation to give 1,2-*dihydronaphthalene*-1,4-*dicarbonyl dichloride* as a pale yellow liquid, $\nu_{max.}$ 1760—1750 cm^{-1} (n.m.r.; see Table 1). Distillation of the liquid at 130°/0·05 afforded a sticky crystalline distillate from which naphthoyl chloride, m.p. 80° (lit.,[27] 80°) was recovered by recrystallisation from ether.

RESULTS AND DISCUSSION

Prior to a comparison of the conformational equilibria of 1,4-disubstituted 1,2-dihydronaphthalenes and 2-substituted 1,2-dihydronaphthalenes, we deemed it necessary to examine the effect of a 4-substituent on the conformation of the partially saturated ring system. To this end the signals assigned to the C-1, C-2, and C-3 protons in the 60 MHz spectrum of 1,2-dihydronaphthalene-4-carboxylic acid (6a) were analysed (AA'BB'C spin system [3]) by iterative computation using the Laocoon III program.[28] Recent analyses of 1,2-dihydronaphthalene (6b) by ourselves [18] and another group [29] render a detailed discussion of the analysis of the spectrum of (6a) unnecessary: the results and computed 'probable errors' of a satisfactory analysis, where all parameters or parameter sets other than $J_{13} = J_{1'3} = 0$ were allowed to vary, are summarised in Table 1. The very large probable errors in the geminal coupling constants reflect the insensitivity of the spectrum to the value of K ($J_{11'} + J_{22'}$) which has been discussed elsewhere.[18,29] The parameters obtained for (6b) are given in Table 1 for comparison.

Lambert [30] has discussed in qualitative terms the relationship between the ratio $J_{trans} : J_{cis}$ (the R-value)

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* Subsequently we refer to this interaction as a *peri* H interation.

† Compound (4a) in refluxing thionyl chloride containing a trace of DMF gives naphthalene-1,4-dicarbonyl dichloride.[21] Thionyl chloride in pyridine is known [22] to be an α chlorinating agent: a similar reaction followed by loss of hydrogen chloride may occur here.

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[28] An improved version of Laocoon II; S. M. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 1964, **41**, 3863.

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[30] J. B. Lambert, *J. Amer. Chem. Soc.*, 1967, **89**, 1836.

TABLE 1

^{1}H N.m.r. parameters obtained for 1,2-dihydronaphthalenes [a]

			δ in Hz downfield from Me_4Si						Coupling constants in Hz											
										J_{cis}		J_{trans}							
Compd.	Substituent	Solvent	1	1'	2	2'	3	4	J_{11}	J_{12}	$J_{1'2'}$	$J_{1'2}$	$J_{12'}$	$J_{22'}$	J_{23}	$J_{2'3}$	J_{24}	$J_{2'4}$	J_{34}
(6*a*)	4-CO_2H [b]	$CDCl_3$	163·34		142·36		442·41		−18·16	6·49		9·16		−20·6	4·84				
			(0·019)		(0·014)		(0·018)		(9·996)	(0·030)		(0·028)		(9·994)	(0·019)				
(6*b*)	[c]	—	152·4		121·8		354·0	385·8	−15·4	7·0		9·4		−16·8	4·3		−1·8		9·4
	[d]	CCl_4	259·81		210·35		581·82	632·50	−15·57	7·09		9·35		−17	4·41		−1·86		9·55
	[e]	CCl_4	156·62		126·27		349·29	379·53	−15·36	7·06		9·37		−17	4·38		−1·81		9·59
(5*a*)	2-CO_2H [f]	$CDCl_3$	305·25	312·07	347·61		607·48	654·99	−15·70	7·01		11·89			3·57		−2·53		9·67
			(0·027)	(0·026)	(0·010)		(0·010)	(0·009)	(0·016)	(0·032)		(0·035)			(0·013)		(0·012)		(0·012)
(5*b*)	2-CO_2Me [g]	$CDCl_3$	298·08	308·44	338·79		603·99	648·27	−15·76	7·18		12·29			3·54		−2·60		9·65
			(0·037)	(0·030)	(0·017)		(0·017)	(0·015)	(0·029)	(0·033)		(0·047)			(0·025)		(0·023)		(0·022)
(5*c*)	2-CO_2Et [h]	$CDCl_3$	299·93	309·30	339·20		606·12	649·94	−15·73	7·02		12·43			3·45		−2·56		9·64
			(0·035)	(0·028)	(0·015)		(0·015)	(0·014)	(0·027)	(0·034)		(0·042)			(0·019)		(0·019)		(0·020)
(5*d*)	2-COCl [i]	$CDCl_3$	310·44	322·26	377·23		605·68	662·45	−15·84	7·14		9·16			4·30		−2·15		9·59
			(0·022)	(0·022)	(0·014)		(0·013)	(0·013)	(0·019)	(0·025)		(0·027)			(0·019)		(0·019)		(0·019)
(4*a*)	1-CO_2H, [j] 4-CO_2H	TFA	393		275	314	744			7·2			3·5	−18·2	3·4	6·3			
(4*b*)	1-CO_2Me, [j] 4-CO_2Me	CCl_4	361		243	281	701			7·0			5·6	−18·0	3·9	5·7			
(4*c*)	1-COCl [k] 4-COCl	$CDCl_3$	407·02		273·99	361·26	757·12			6·94			3·38	−18·16	3·27	6·41			
			(0·016)		(0·017)	(0·017)	(0·016)			(0·023)			(0·024)	(0·023)	(0·024)	(0·026)			

[a] Values in parentheses are computed ' Probable Errors of Parameter Sets.' [b] At 60 MHz, 40 lines fitted to 25 observed transitions to within 0·17 Hz, rms 0·073. [c] At 60 MHz, data from ref. 18. [d] 100 MHz, data from ref. 29. [e] At 60 MHz, data from ref. 29. [f] At 100 MHz, 69 lines fitted to 30 observed transitions to within 0·10 Hz rms 0·046. [g] At 100 MHz, 54 lines fitted to 27 observed transitions to within 0·17 Hz rms 0·064. [h] At 100 MHz, 58 lines fitted to 30 observed transitions to within 0·19 Hz rms 0·058. [i] At 100 MHz, 79 lines fitted to 31 observed transitions to within 0·17 Hz rms 0·073. [j] At 100 MHz, data from ref. 18. [k] At 100 MHz, 32 lines fitted to 24 observed transitions to within 0·12 Hz rms 0·053.

and conformation for a wide range of six-membered ring compounds including some containing sp_2 hybridised carbon atoms. Buys [31] has provided a quantitative extension from which the dihedral angle in a CH_2–CH_2 fragment can be calculated and the agreements between the structural data obtained by the *R*-value method and *X*-ray analysis are generally very satisfactory.[32] The *R*-values for the CH_2–CH_2 fragments in (6a) and (6b) correspond to dihedral angles of 50 and 51° respectively from which we conclude that to a first approximation the 4-carboxy-group does not distort the saturated part of the ring. To our knowledge, no other structural determinations have been performed on 1,2-dihydronaphthalene but a value of 45° has been derived from microwave data [4] for the corresponding angle in 1,3-cyclohexadiene and this has lately received theoretical support from Hendrickson type calculations.[33] The differences in $J_{12(cis)}$ and $(J_{23} + J_{2'3})/2$ in (6a) and (6b) may be attributable to electronegativity effects but we do not wish to pursue this at the present time.

The n.m.r. spectra of (5a—d) were recorded at 100 MHz and in each case the signals assigned to the two C-1 protons absorb upfield from the strongly coupled signal for the C-2 proton. Of the vinyl proton signals the lower field doublet of doublets is assigned to the C-4 proton, *cf.* 1,2-dihydronaphthalene.[18,29] Ignoring long-range coupling to the aryl protons and assuming $J_{13} = J_{1'3} = J_{14} = J_{1'4} = 0$ and negative values for geminal and allylic coupling constants the spectra arising from the dihydro-ring protons in (5a—d) were analysed by ABCDE theory. The analyses gave a good fit between the experimental and theoretical spectra for each compound. The RMS errors were less than 0·08 and error in line positions were 0·19 Hz or less.

The 60 MHz spectrum of the acid (5a) was also examined but a number of low-intensity transitions associated with the C-1 protons were obscured by the signals from the C-2 proton which rendered the spectrum difficult to analyse satisfactorily. The ' stick plot ' and simulated 60 MHz spectra calculated from the parameters obtained from the analysis of the 100 MHz spectrum are in good agreement with the experimental 60 MHz spectrum (Figure).

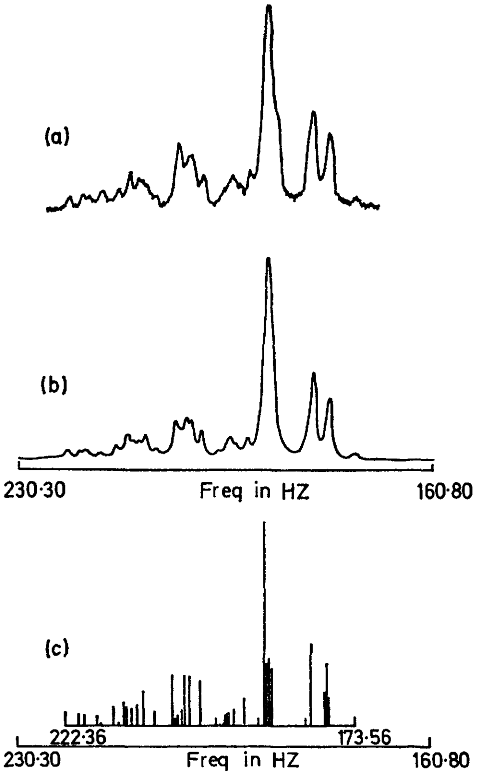

FIGURE (a) 60 MHz Spectrum of the protons at C-1 and C-2 in 1,2-dihydronaphthalene-2-carboxylic acid. (b) and (c) Simulated and stick-plot spectra of the same protons (at 60 MHz) calculated from the analysis of the 100 MHz spectrum of the acid. Spectrum (a) is offset 2·8 Hz downfield to align with (b) and (c)

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[31] H. R. Buys, *Rec. Trav. chim.*, 1969, **88**, 1003.

[32] For a survey see, J. B. Lambert, *Accounts Chem. Res.*, 1971, **4**, 87.

[33] G. Favini, F. Zuccarello, and G. Buemi, *J. Mol. Struct.*, 1969, **3**, 385.

In each of (5a—d) J_{12} is assumed to be a *cis*-coupling because it is very similar within the series and similar to the *cis*-couplings in the 1,4-disubstituted 1,2-dihydronaphthalenes.[18] From the *trans*-coupling $J_{1'2}$, information about the conformational equilibrium can be obtained since $J_{1'2} = xJ_{ee} + (1 - x)J_{aa}$, where x is the fraction of the compound existing with the substituent pseudo-axial. The similarity of $J_{1'2}$ [$(J_{aa} + J_{ee})/2$] in (6a) and (6b) is in accord with the assumption that J_{aa} and J_{ee} have the same values in both the 2-substituted series and the 1,4-disubstituted series where values of $J_{ee} = 2$ and $J_{aa} = 16{\cdot}5$ Hz were earlier deduced [18] from a consideration of model compounds and literature data. For both series we now favour however a value of 16 Hz for J_{aa} because a value for $(J_{aa} + J_{ee})/2$ of *ca.* 9·0 Hz has since been derived [34]* for the 1,4-disubstituted series and a lower value is in closer agreement with the value of J_{aa} in a similar system.[35] Using $J_{ee} = 2$ and $J_{aa} = 16$ Hz † we evaluated x and $\Delta G°$ for the conformational equilibria of (5a—d) and (4a—b) (Table 2). The recalculated x values for (4a) and (4b) are within 1% of those obtained earlier [18] ($\Delta G°$ within 0·1 kcal/mol).

TABLE 2

Conformational equilibrium data for substituted 1,2-dihydronaphthalenes

Compd.	Substituent group	Solvent	x (% Axial subst.)	$\Delta G°$ (kcal/mol)
(5a)	2-CO_2H	$CDCl_3$	29	0·5
(5b)	2-CO_2Me	$CDCl_3$	27	0·6
(5c)	2-CO_2Et	$CDCl_3$	26	0·7
(5d)	2-COCl	$CDCl_3$	49	0·0
(4a)	1-CO_2H(4-CO_2H)	TFA	89	−1·3
(4b)	1-CO_2Me(4-CO_2Me)	CCl_4	74	−0·7
(4c)	1-COCl(4-COCl)	CCl_4	90	−1·4

J_{23} And J_{24} are also conformationally dependent coupling-constants and extrapolation of the results for (5a—d) leads to values of 2·6 and 6·0 Hz for J_{2a3} and J_{2e3} and −3·2 and −1·0 Hz for J_{2a4} and J_{2e4}, respectively.

Although coupling constants between vicinal and allylic protons are subject to influences other than dihedral angle a comparison between the derived values and those predicted from empirical or theoretical derivations of the angular dependence of $J_{vic}(\mathrm{CH{-}\overset{\|}{C}{-}H}$ type) and J_{allyl} is instructive. Inspection of molecular models suggests that the C(2)–H_{ax} bond is approximately at right angles to the plane of the C(3)–C(4) bond [the dihedral angle between the C(1)–C(2) and C(5)–C(6) bonds in 1,3-cyclohexadiene has been calculated [33] to be 31°] and contributions from π terms to J_{2a3} and J_{2a4} should be approaching a maximum. From Garbisch's [36] relationship for $J_{vic}(\mathrm{CH{-}\overset{\|}{C}{-}H})$ and an inspection of Sternhell's curve [37] for transoid allylic coupling constants, the values predicted for J_{2a3}, J_{2e3}, J_{2a4}, and J_{2e4} are *ca.* 2·6, *ca.* 5·6, *ca.* −3, and *ca.* 0 Hz, respectively. The magnitude of J_{allyl} in the region of $J = +5$ to $-1{\cdot}5$ Hz is very sensitive to small variation in angle. The agreement between our derived coupling constants and the predicted coupling constants we believe provides independent support for the validity of our conformational equilibrium data in Table 2 and accordingly, the values chosen for J_{aa} and J_{ee}.

The results in Table 2 show that the carboxy and alkoxycarbonyl groups which preferentially occupy the pseudo-axial site in the 1-position are preferentially pseudo-equatorial in the 2-position in spite of the absence of destabilising 1,3-diaxial interactions with protons. The $\Delta G°$ values for (5a—c) are *ca.* 0·6 kcal/mol less than for the corresponding cyclohexyl derivatives [38] but rigorous comparisons are precluded because the dihedral angles in the two ring systems differ. Within the dihydronaphthalene ring, differences in the bond-lengths of the two unsaturated bonds of the dihydro-ring should not render the pseudo-axial and pseudo-equatorial sites of the 1-position significantly different from those of the 2-position. The difference in ΔG of 1·3 kcal/mol for a $-CO_2Me$ group in the 1- and 2-positions must then arise from the difference in interactions of a pseudo-equatorial substituent with the C-8 hydrogen compared with a vinyl hydrogen. [Compounds (4a) and (5a) are not comparable because the results were obtained in very dissimilar solvents.] The destabilisation of pseudo-equatorial substituents by aromatic *peri* hydrogen interactions is analogous to $A_{1,3}$ strain [39] and evidently dominates the conformational equilibria of systems such as 9-substituted 9,10-dihydroanthracenes.[40]

Unlike the 2-carboxy and 2-alkoxycarbonyl groups the 2-COCl substituent in (5d) shows no preference for either the pseudo-axial or pseudo-equatorial site. This dissimilarity is in marked contrast to the cyclohexyl series where these substituents are reported to have very similar equatorial preferences [38] and with this in mind we examined the conformational equilibrium of 1,2-dihydronaphthalene-1,4-dicarbonyl dichloride (4c). The signals in the 100 MHz spectrum were readily assigned and analysed by ABCD theory (Table 1): as before, the conformational equilibrium was evaluated by comparing $J_{1'2}$ with $J_{aa} = 16$ and $J_{ee} = 2$ Hz (Table 2). Comparison of the results for (4c) with those for the ester (4b) shows that the overall conformational requirements of the COCl and CO_2Me groups are quite different in the 1 position also, the pseudo-axial preference of the former being greater. (A similar comparison for the CO_2H group is again invalid.) The difference in ΔG

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* In ref. 34 compounds (I) and (II)—the bisester (4b) and the bisacid (4a)—are erroneously referred to as 1-carbomethoxy and 1-carboxy-1,2-dihydronaphthalenes.

† Limited solubility prevented us measuring spectra of the conformationally biased compounds at very low temperatures; such spectra could have provided further information about these values.

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values for the 1-COCl and 2-COCl groups, 1·4 kcal/mol, is the same within experimental error to that between the ΔG values for the 1- and 2-CO_2Me groups which we believe may imply a specific value for the destabilising interaction between the C-8 H and an equatorial 1-COX function.

CONCLUSION

1,2-Dihydronaphthalene-2-carboxylic acid and its methyl and ethyl esters exist (in $CDCl_3$ solutions) with the substituents predominantly pseudo-equatorial but the corresponding acid chloride shows no conformational preference. The pseudo-axial preferences observed for substituents in the 1-position are best interpreted in terms of *peri* H interactions.

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