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The γ- and the δ-effects in ^{13}C NMR spectroscopy in terms of nuclear chemical shielding (NCS) analysis

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epoc ABSTRACT: Carbon-13 NMR is widely used in the determination of the stereochemistry of organic compounds. Changes in chemical shifts caused by interactions of groups that are close in space normally result in shielding of the carbon and deshielding of the hydrogen nuclei that are involved. This is not always the case, however, and further work on the origin of these effects would be desirable. Early applications of theoretical methods to the study of NMR shielding parameters were not particularly successful, but in recent years, the calculation of NMR shielding parameters by theoretical methods has developed into a useful and popular tool for structural studies by NMR. A promising approach to the problem of distinguishing and evaluating stereochemical influences on carbon and hydrogen chemical shifts is provided by natural chemical shielding (NCS) analysis. This method allows a partitioning of theoretical NMR shieldings into magnetic contributions from bonds and lone pairs of the molecule using the natural bond orbital (NBO) method. In order to investigate the origins of steric effects, we employed the NCS analysis to axial/equatorial-Me-cyclohexane, norbornane and *exo*/*endo*-Me-norbornane, in addition to *n*-pentane in the *anti*, *gauche* and $g^P g^M$ conformations. Our results indicate that distortions in molecular structure due to steric effects can result in bond stretching or compression or in angular distortions. Changes in bond lengths result in the predictable shielding or deshielding of the nuclei that are involved. Where the molecular framework may be distorted to alleviate strain, chemical shifts appear to reflect changes in angles. Copyright © 2004 John Wiley & Sons, Ltd.
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KEYWORDS: ^{13}C NMR spectroscopy; γ- and δ-effects; steric hindrance; partitions to natural chemical shieldings

INTRODUCTION

The widespread use of ^{13}C NMR spectroscopy in the determination of the stereochemistry of organic compounds is based on changes in chemical shifts caused by groups that are close in space. Their interactions normally result in shielding of the carbon and deshielding of the hydrogen nuclei that are involved. However, since this is not always the case,[1] it seems that further theoretical and experimental work would be desirable in order to trace the origin of these effects.

Nuclear magnetic shielding constants were identified and analysed over 40 years ago. However, because of practical problems associated with the calculation of this property, the early applications of theoretical methods to the study of NMR shielding parameters were not particularly successful. In recent years, these obstacles have been overcome, partly as a result of a general improvement in quantum mechanical techniques and computer technology and partly through the development of special methods and programs for the calculation of NMR properties. As a result, over the last 5–10 years, the calculation of NMR shielding parameters by theoretical methods has developed into a useful and popular tool of computational quantum chemistry,[2] and several laboratories have made use of theoretical methods to investigate the structural and conformational dependences of ^{13}C NMR chemical shifts and substituent effects.[3–9]

The interpretation of ^{13}C and ^{1}H NMR spectra of tetracyclododecane[10] confirmed some of the earliest work[11] related to steric effects on chemical shifts. Comparison of tetracyclic norbornyl systems with their bicyclic counterparts clearly shows that, in all cases in which significant van der Waals interactions might be expected, shielding is observed for carbon atoms and deshielding is observed for hydrogen atoms. Force field calculations revealed a significant shortening of the compressed C—H bond,[10] in line with the theoretical analysis of strain in cyclic hydrocarbons since, in CH_2 groups subjected to strain, charge is transferred from hydrogen to carbon, increasing the s-character of the C—H bond.[12,13] On the other hand, the *ab initio* IGLO MO work of Barfield and co-workers on paramagnetic bond contributions to carbon-13 chemical shifts was used to examine the torsion angle [φ about C(2)—C(3)] dependence of α-, β- and γ-effects for *n*-butane.[7] Satisfactory

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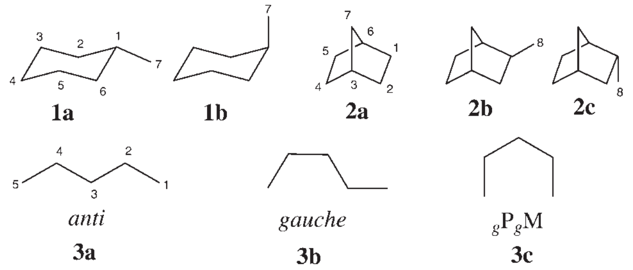
agreement was found with the experimental data for *n*-butane but not for the methyl-substituted bicyclic compounds with reasonably well defined geometries. Extension of the analysis of γ-effects led to satisfactory agreement with the experimental data (for several series of methyl-substituted bicyclic compounds). A subsequent IGLO study of *n*-pentane and three substituted butanes (X = CN, OH, F) examined the dependence of α-, β-, γ- and δ-effects on the torsion angles φ_1 and φ_2 about the C(1)—C(2) and C(2)—C(3) bonds, respectively.[8] In contrast to β-effects, which were found to be almost independent of φ_2, the calculated α-, γ- and δ-effects showed substantial variations with both dihedral angles. The predicted dependences of substituent and conformational effects were consistent with the experimental results for several series of substituted bicyclo[2.2.1]heptanes, bicyclo[2.2.2]octanes and *trans*-decalins. Fisher and Gradwell[14] similarly noted a correlation between dihedral angles and substituent effects on hydrogen chemical shifts. How, then, can these stereochemical influences on ^{13}C and ^{1}H chemical shifts be distinguished and evaluated?

A promising approach to this problem is provided by natural chemical shielding (NCS) analysis.[15] This method allows a partitioning of theoretical NMR shieldings, calculated by gauge including atomic orbitals (GIAO), into magnetic contributions from bonds and lone pairs of the molecule using the natural bond orbital (NBO) method. In addition to computing the contributions to shielding from localized (or 'Lewis') bonds, this approach also computes those of a delocalized (or 'non-Lewis') nature.[15]

A good example of the application of NCS analysis to chemical shifts of saturated hydrocarbons is provided by cyclohexane.[16] The difference in chemical shifts of axial and equatorial hydrogens had long been attributed to the anisotropic effect of the C—C single bond. As result of the NCS analysis, calculated in that study,[16] the various contributions to theoretical NMR shieldings of the axial/equatorial protons of cyclohexane were obtained; actually, the contributions of the C(2)—C(3) and C(5)—C(6) bonds to the theoretical shieldings of the C(1)—H_{eq}/H_{ax} protons determine both position and chemical shift difference of the two protons (dominated by hyperconjugation).

In order to investigate the origins of steric effects, we applied NCS analysis to systems for which these effects make significant contributions to chemical shifts; especially the various partitions of the bonds to the NCS of ^{13}C nuclei in γ- but also δ-fragments were considered (Scheme 1).

Scheme 1



Scheme 2

The aim of this work was to establish with the help of NCS analysis why these two effects in ^{13}C NMR spectroscopy, even if being sterically very similar, proved to be of reversed sign (γ-*gauche* effect to high field and δ-*syn*-axial effect to low field). A number of simple molecules were studied for this purpose: axial/equatorial-Me-cyclohexane, norbornane and *exo*/*endo*-Me-norbornane, and *n*-pentane in the *anti*, *gauche* and $g^P\,g^M$ conformations (Scheme 2).

RESULTS AND DISCUSSION

Our preliminary results using MM2 methods indicated that distortions in molecular structure due to steric effects can result in bond stretching or compression or in angular distortions.[13] Changes in bond lengths lead to C—H bond polarization and the type of steric effect that was originally invoked to account for changes in chemical shifts and were detected for rigid policyclic systems.[11] Where the molecular framework may distort to alleviate strain, chemical shifts appeared to reflect changes in angles of the type investigated by Barfield's group.[3–8]

For cyclohexane (**1**) and norbornane (**2**) derivatives, our present theoretical values of both δ and also $\Delta\delta$, calculated by the GIAO method, are in good agreement with the observed shielding or deshielding and their relative magnitudes. This is also the case for the corresponding ^{13}C chemical shifts of *n*-pentane in the three conformations that reflect other structures of interest (cf. Table 1).[17] These results indicate that the calculations that were used are in line with the available experimental data on the molecules that were selected.

γ-Effects

Substituent effects $\Delta\delta_i$ ($i = \alpha$, β, γ, δ, ε, etc.) in the ^{13}C NMR spectra of aliphatic and alicyclic compounds are the changes in chemical shifts $\Delta\delta_i$ of carbon C_i which occur on replacing a hydrogen atom at the C_α carbon by a substituent X. Empirical additivity relationships based on the tabulated substituent effects are very useful in the interpretation of ^{13}C NMR spectra. The relationship between γ- and δ-substituent effects and stereochemical

Table 1. Comparison of experimental and theoretical ^{13}C chemical shifts of **1–3**

Substance	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
1a	33.1 (27.1)[a]	35.8 (29.9)	26.7 (23.2)	26.7 (22.9)	26.7 (23.2)	35.8 (29.9)	22.9 (22.2)	
1b	27.7 (23.5)	32.1 (27.2)	20.8 (18.7)	27.4 (23.2)	20.8 (18.7)	32.1 (27.2)	17.5 (17.8)	
	$\Delta\delta$ −5.4 [−3.6][b]	−2.7 [−2.7]	−5.9 [−4.3]	+0.7 [+0.3]	−5.9 [−4.5]	−2.7 [−2.7]	−5.4 [−4.4]	
2a	36.3 (32.1)	29.6 (26.1)	29.6 (26.1)	36.3 (32.1)	29.6 (26.1)	29.6 (26.1)	38.3 (34.3)	
2b	36.9 (32.5)	39.8 (33.8)	36.4 (30.8)	43.0 (37.2)	30.0 (27.0)	28.7 (25.3)	34.8 (31.7)	22.3 (21.3)
	$\Delta\delta$(**2a–b**)							
	+0.6 [+0.4]	+9.8 [+7.7]	+6.8 [+4.7]	+6.7 [+5.1]	+0.4 [+0.9]	−0.9 [−0.8]	−3.5 [−2.6]	
2c	37.7 (32.7)	38.4 (32.5)	34.0 (29.0)	41.7 (36.5)	22.1 (20.4)	30.2 (26.4)	(35.7)	17.4 (17.6)
	$\Delta\delta$(**2b–2c**)							
	+0.8 [+0.2]	−1.4 [−1.3]	−2.4 [−0.9]	−1.3 [−0.7]	−7.9 [−6.6]	+1.5 [+1.1]	[+4.0]	−4.7 [−3.7]
3a	(15.6)	(22.5)	(31.0)	(22.5)	(15.6)			
3b	(11.5)	(15.8)	(23.8)	(17.7)	(15.8)			
	$\Delta\delta$(**3a–b**)	—	—	—	−4 to −6.6			
	[−3.9]	[−6.7]	[−7.2]	[−4.8]	[+0.2]			
3c	(14.9)	(18.2)	(16.7)	(18.2)	(14.9)			
	$\Delta\delta$(**3a–3c**)	—	—	—	—			
	[−0.7]	[−4.3]	[−14.3]	[−4.3]	[−0.7]			
	$\Delta\delta$(**3b–3c**)	—	—	+0.2 to + 1.2	+2.2 to + 4.7			
	[+3.4]	[+2.4]	[−7.1]	[+0.5]	[−0.9]			

[a] In parentheses: calculated δ values.

[b] In square brackets: calculated $\Delta\delta$ values.

features were recognized at an early stage, and the conformational implications of the various substituent effects were revealed to be of particular interest.[18]

The consequences of steric interactions can be exemplified by the γ-effect. The introduction of a methyl group in a cyclic molecule leads to new interactions with a neighbouring hydrogen atom, resulting in shielding of the carbon nuclei that are involved. In Table 2 the chemical shift variations ($\Delta\delta_i$), due to additional γ- and δ-substituent effects, are compared with the results of the corresponding NCS analysis, in which only the most significant contributions to the natural chemical shieldings $\Delta\sigma_i$ of the ^{13}C nuclei of interest are included. For these systems, the calculated $\Delta\sigma_i$ substituent effects are due to contributions only from the bonds to the carbon atom that is involved in the steric interaction, the C(γ)—C and C(γ)—H bonds. This is the case for the terminal methyl carbons [in the case of *exo*/*endo*-Me-norbornane, the C(2)—H(*exo*) bond also contributes to some extent], whereas for methylene carbons, besides the C—C bond only the C(γ)—H bonds and not those attached to adjacent carbon atoms contribute significantly.

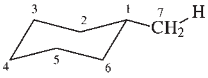
The sum of these C(γ)—C and C(γ)—H contributions to the γ-carbon chemical shieldings corresponds to the chemical shift difference between the two conformations even though all other bonds of the molecule contribute likewise (but, obviously, compensate each other). The C(γ)—C bond lengthens, while the corresponding C(γ)—H bonds are shortened (cf. Table 2) in order to avoid steric strain. Even though the magnitudes of variations in bond lengths of the various γ-fragments are different, this effect is generally observed. Thus, the NCS analysis is in line with the γ-effect leading to shielding when steric hindrance in the γ-fragments increases. Similar considerations apply to changes in bond angles: cyclohexanes [C(2)—C(3)—H(ax) increases by 0.8° in **1(ax)** with respect to **1(eq)**]; norbornanes [comparing **2a** and **2b**, both C(6)—C(7)—H(7*syn*) and C(1)—C(6)—C(7) bond angles open by 0.6° and 1.05°, respectively—comparing **2b** and **2c**, the two C(6)—C(5)—H(5*endo*) and C(1)—C(6)—C(5) bond angles are widened by 1° and 2.7°, respectively, but the two angles C(6)—C(7)—H(7*syn*) and C(1)—C(6)—C(7) will be correspondingly reduced by −0.6° and −1.75°, respectively—the angles C(6)—C(7)—H(7*anti*) and C(1)—C(6)—C(7) proved to be influenced only negligibly]; *n*-butanes [C(3)—C(4)—C(5) increases by 4.15° when comparing *anti* and *gauche* conformations].

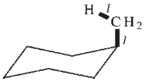
δ-Effects

There are two variants of the δ-effect (cf. Scheme 3). In the first case (i), the terminal atom C(1) is not shifted to lower field significantly but by −0.7 ppm to higher field. A high-field shift of $\sigma = 0.24$ ppm is calculated but arising from the C(4)—C(5) bond (2.88 ppm), slightly compensated by a deshielding effect of two C(5)—H bonds. However, C(4) is strongly shifted to high field (by −4.27 ppm), due only to the C(2)—C(3) bond, respectively, deshielding $\sigma_{C(4)}$ by +4.37 ppm.

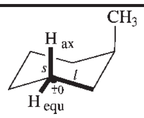
It is worth pointing out that it is not the terminal carbons in δ-fragments which will be shifted to lower field, if the 1,3-*syn*-axial conformation is established. Carbons in the inner fragment are influenced but shifted (not suprisingly) to high field by ca 4.5 ppm. The same is true for the other inner carbon atom C-3 ($\Delta\delta = -14.3$ ppm; cf. Table 1) but here they are

Table 2. Changes in bond lengths and partitions to the chemical shielding tensor of various ^{13}C nuclei in **1–3** (*l*, lengthening; *s*, shortening)

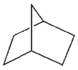
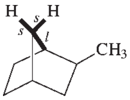




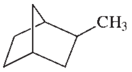
δ(C7) 22.22 ppm	17.78 ppm	*Δδ = −4.44 ppm*
C(1)–C(7)		Δσ
−12.04	−8.89	+3.15
−0.88	−1.46	−0.58
C(7)–H		
−2.52	−0.73	+1.79
0.46	0.21	*−0.25*
		Δσ = +4.11 ppm

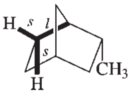


δ(C3) 23.24 ppm	18.74 ppm	*Δδ = −4.5 ppm*
C(2)–C(3)		Δσ
−7.70	−6.36	+1.34
−0.76	−0.99	−0.23
C(3)–H(11)(*ax*)		
−3.16	−1.54	+1.62
0.87	0.79	−0.08
C(3)–H(12)(*eq*)		
−4.36	−3.59	0.77
0.19	0.10	*−0.09*
		Δσ = +3.33 ppm

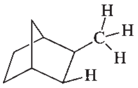



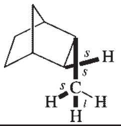
δ(C7) 34.26 ppm	31.69 ppm	*Δδ = −2.57 ppm*
C(6)–C(7)		Δσ
−9.55	−8.37	+1.18
−0.66	−0.78	−0.12
C(7)–H(7*syn*)		
−7.52	−5.97	+1.55
0.71	0.72	*+0.01*
		Δσ = 2.84 ppm





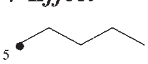
δ(C5) 27.0 ppm	20.36 ppm	*Δδ = −6.6 ppm*
C(5)–C(6)		Δσ
−9.18	−7.11	+2.07
−0.66	−1.15	−0.49
C(5)–H(5*endo*)		
−5.71	−4.17	+1.55
0.61	0.61	+0.01
C(5)–H(5*exo*)		
−4.59	−2.54	+2.05
0.28	0.53	*+0.25*
		Δσ = +5.43 ppm

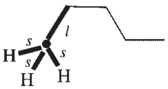




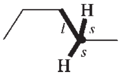
δ(C8) 21.27 ppm	17.56 ppm	*Δδ = −3.71 ppm*
C(1)–C(8)		Δσ
−10.84	−10.24	+0.6
−1.51	−1.70	−0.19
C(2)–H(12)		
−0.63	0.15	+0.78
−0.09	0.01	+0.1
C(8)–H(20)		
−4.17	−1.97	+2.2
0.30	−0.64	− 0.94
C(8)–H(22)		
−1.81	−1.17	+0.64
0.43	0.32	*−0.09*
		Δσ = +3.1 ppm

γ-Effect





δ(C1) 15.63 ppm	11.52 ppm	*Δδ = −4.11 ppm*
C(1)–C(2)		Δσ
−10.55	−7.65	+2.90
−1.07	−1.73	−0.66

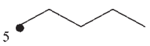



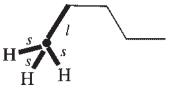
δ(C4) 22.47 ppm	17.68 ppm	*Δδ = −4.81 ppm*
C(4)–C(3)		Δσ
−10.15	−8.23	+1.92
−0.69	−1.14	−0.45

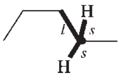
Continues

Table 2. Continued

γ-Effect

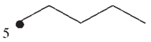


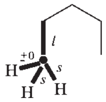


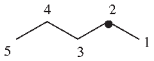


δ(C1) 15.63 ppm	11.52 ppm	*$\Delta\delta = -4.11$ ppm*	δ(C4) 22.47 ppm	17.68 ppm	*$\Delta\delta = -4.81$ ppm*
C(1)–H(15)			C(4)–H(9)		
−1.05	−0.60	+0.45	−2.69	−1.72	+0.97
+0.16	+0.03	−0.13	0.79	+0.68	−0.11
C(1)–H(16)			C(4)–H(10)		
−2.44	−2.63	−0.19	−2.69	−1.72	+0.97
−0.02	+0.34	+0.36	0.79	+0.68	*+0.11*
					$\Delta\sigma = +3.19$ ppm
C(1)–H(17)					
−1.05	−0.60	+0.46			
+0.16	+0.03	*−0.13*			
		$\Delta\sigma = +3.06$ ppm			

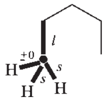
δ-Effect







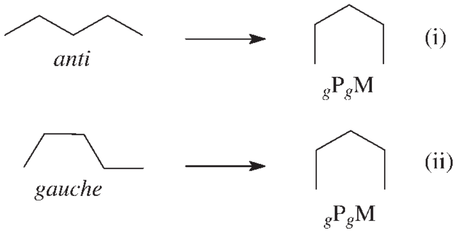
δ(C1) 15.63 ppm	14.9 ppm	*$\Delta\delta = -0.73$ ppm*	δ(C4) 22.47 ppm	18.20 ppm	*$\Delta\delta = -4.27$ ppm*
C(1)–C(2)		$\Delta\sigma$	C(2)–C(3)		$\Delta\sigma$
−10.55	−7.67	+2.88	−10.15	−5.56	+4.59
−1.07	−1.60	−0.53	−0.69	−0.91	*−0.19*
					$\Delta\sigma = +4.37$ppm
C(1)–H(15)					
−1.05	−1.61	−0.56			
0.16	0.0	−0.16			
C(1)–H(16)					
−2.44	−3.5	−1.06			
−0.02	+0.37	+0.39			
C(1)–H(17)					
−1.05	−1.61	−0.56			
0.16	0.00	*−0.16*			
		$\Delta\sigma = 0.24$ ppm			



δ(C1) 11.52 ppm	14.87 ppm	*$\Delta\delta = +3.35$ ppm*
C(1)–H(15)		$\Delta\sigma$
−0.60	1.61	−1.01
0.03	0.0	−0.03
C(1)–H(16)		
−2.63	−3.5	−0.87
0.34	+0.37	+0.03
C(1)–H(17)		
−0.60	−1.61	−1.01
0.03	0.00	*+0.03*
		$\Delta\sigma = -2.86$ ppm

subjected to the much stronger effects of the two sides of the symmetrical δ-1,3-diaxial fragment. Hence, as a first result, there is no low-field shift effect at all in the δ-1,3-diaxial fragment, only strong high-field shifts in the γ-fragments involved, as is usual for a kind of system which is strongly sterically hindered.

As for the second case (ii) (cf. Scheme 3), when comparing *gauche*-pentane with $g^P g^M$-pentane (δ-1,3-diaxial fragment), the chemical shift variations seem very familiar (cf. Table 2). The terminal atom C(1) ($\Delta\delta = +3.35$ ppm) becomes deshielded. Sources are mainly partitions of the C(1)—H bonds of this terminal methyl group, deshielding C-1 together by $\Delta\sigma$ ca 3 ppm (in fair aggrement with the experiment). The inner carbon atoms C(2)/C(4) are not influenced by this conformational change [deshielding contributions of



Scheme 3

C(2)/C(3)—H bonds are balanced by shielding contributions arising from C(1)—C(2)/C(4)—C(5) bonds and the terminal C—H and the C(2)—C(4)—H bonds, respectively]. Only C(3) is significantly shifted ($\Delta\delta = -7.1$ ppm; cf. Table 1) to high field, reflecting the steric strain present in this δ-fragment.

The corresponding bond lengths and bond angles behave as expected if steric strain increases: C—C bonds become longer and C—H bonds correspondingly shorter in order to avoid the steric strain and the C(3)—C(4)—C(5) bond angle increases by 9.55° if *anti* and $g^P g^M$ conformers are compared and by 5.3° if *gauche* and $g^P g^M$ conformers are compared, both in precise agreement with the enormous increase in steric strain in the δ-syn-axial fragment.

This result further supports the former finding that there is no systematic low field δ-effect in δ-syn-axial conformations. Only if *gauche*-pentane conformers are compared with the corresponding $g^P g^M$ conformer with respect to changes in the ^{13}C chemical shifts is there a low-field shift of the terminal carbons. However, it arises from nothing more than the comparison of two specific conformations, and it is not certain.

Another very interesting result arises from the NCS analysis of the ^{13}C chemical shifts of the carbon atoms involved in the γ- and δ-fragments studied. Even if in these strongly sterically hindered fragments the ^{13}C chemical shifts of just about all carbon atoms involved will be influenced, the contributions to the corresponding chemical shieldings arise from C—C and C—H bonds including the carbon atom studied (cf. Scheme 2). Obviously, only these are changed significantly owing to the steric hindrance in the γ- and δ-fragments, and are responsible for the chemical shift changes of different signs for γ- and δ-effects observed in ^{13}C NMR spectroscopy. Hence, the steric hindrance within the fragment studied is not the real source of the sign of the γ- and δ-effects but their sign can be partitioned into the natural chemical shiedings of the relevant carbon atoms studied.

Computational method

Ab initio quantum mechanical calculations were performed on SGI Octane and SGI Origin 2000 workstations using the Gaussian 98 program.[19] Geometry optimization was performed at the HF/6–31G* level of theory without constraints.[20] Shieldings were calculated using the gauge-independent atomic orbital (GIAO) method[21,22] as incorporated in Gaussian 98[15] at the same level of theory.

The NBO 5.0 program[15] was utilized by linking it directly to the Gaussian 98 program.[19] The NCS–NBO analyses partitioned quantitatively the shielding of a particular nucleus into magnetic contributions from all bonds and lone pairs present in the structures, the shielding and deshielding contributions being divided into Lewis and non-Lewis components.

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