

## Carbon-13 Chemical Shifts of 4-Substituted Tricyclenes

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<sup>13</sup>C Chemical shifts of a series of 4-substituted tricyclenes (1)–(10) are reported and are considered in relation to substituent effects and related structures. Chemical shifts of C(4) and the equivalent C(2) and C(6) cyclopropyl carbons correlate empirically with the electronegativity parameter,  $E_R$ . Smaller low-field  $\beta$ -shifts observed for C(3) and C(5) of the tricyclenes with respect to adamantanes (10) when the bridgehead substituent contains more than one atom heavier than hydrogen are rationalised in terms of the distances over which the diamagnetic shielding component of these structures has to operate. A good correlation is obtained between the substituent induced shifts of the exocyclic methyls C(10) and the equivalent pair C(8) and C(9) which are respectively to low and high field. The directions of these shifts extends a previously noted pattern for methyl induced shifts. <sup>13</sup>C Shift data are reported for a limited number of 1-substituted bicyclo[2.2.2]octanes.

THE use of bridgehead substituted bicyclic compounds provides a convenient method of elucidation of factors which affect <sup>13</sup>C chemical shifts in aliphatic systems. Such an approach reduces the importance of 1,4-interactions between the substituent and ring members which are known to lead to appreciable diamagnetic effects. To this end Lippmaa and his co-workers<sup>1</sup> have studied the <sup>13</sup>C chemical shift variation of ring carbons in a series of 1-substituted adamantanes (11) and have derived substituent <sup>13</sup>C chemical shift increments for carbons  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  to the C(1) bridgehead substituent. Also Maciels's group<sup>2</sup> has examined the chemical shift behaviour of a limited number of 1-substituted bicyclo[2.2.2]octanes; assignments were supported by specific deuteration of a methylene carbon.

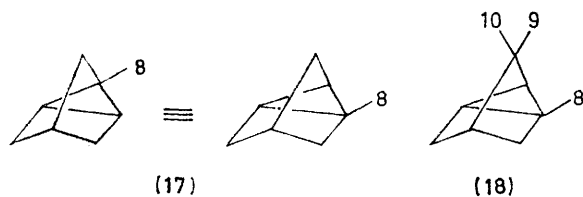
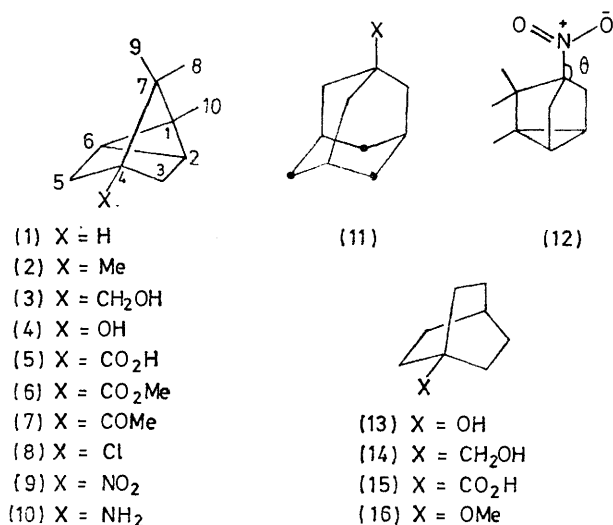
<sup>1</sup> T. Pehk, E. Lippmaa, V. V. Sevostjanova, M. M. Krayuschkin, and A. I. Tarasova, *Org. Magnetic Resonance*, 1971, **3**, 783.

In the present work we have synthesised a series of 4-substituted tricyclenes (1)–(10), and have examined their <sup>13</sup>C n.m.r. spectra with particular reference to chemical shift variation of ring carbons with the nature of the C(4) substituent. Tricyclenes were chosen for investigation rather than nortricyclenes on grounds of their readier synthetic accessibility. In addition the two types of exocyclic methyl group offered a further basis for examination of C(4) substituent induced chemical shift variation as regards the methyl groups themselves, the secondary and quaternary  $\beta$ -carbons, and the tertiary and quaternary cyclopropyl  $\gamma$ -carbons.

The geometry of the strained tricyclo[2.2.1.0<sup>2,6</sup>]-heptane ring skeleton is known from an electron

<sup>2</sup> G. E. Maciel and H. C. Dorn, *J. Amer. Chem. Soc.*, 1971, **93**, 1268.

diffraction study of 1-chloronortricyclene.<sup>3</sup> This strained ring skeleton is probably rigid and is considered to be



essentially unaffected either by introduction of three methyl groups to give tricyclene or by variation of the C(4) bridgehead substituent in tricyclene.

<sup>13</sup>C Chemical shifts are influenced by a screening constant which is composed of (a) a local diamagnetic term, (b) a local paramagnetic term, and (c) a term which represents screening due to electronic circulations in the rest of the molecule.<sup>6</sup> The influence of the diamagnetic term is considered to be insignificant and the paramagnetic term is considered to be the major factor which influences chemical shifts and greatest importance is attached to variation in the electronic environment of the carbon atom. Diamagnetic effects are predicted to result from a substituent induced increase in electron density or steric polarisation along a C-H bond, and paramagnetic shifts result from the presence of low lying excited states.

Since tricyclene possesses a plane of symmetry through C(1), C(7), and C(4), the <sup>13</sup>C n.m.r. spectra of tricyclenes (1)–(10) are characterised by seven absorptions (in addition to those of the substituent itself). Assignments are supported by proton off-resonance decoupled spectra. Absorptions in the range 9.4–10.2 p.p.m. are attributable to C(10) and the more intense absorptions in the range 17.3–19.4 p.p.m. are assigned to the equivalent C(8) and C(9). Of C(1), C(4), and C(7) which give singlets in the off-resonance spectrum the cyclopropane C(1) absorbs in the range 26.3–29.8 p.p.m. and the C(7) gem-dimethyl-bearing carbons absorb between 43.1 and 47.7 p.p.m. whereas the response of C(4) to substituent variation is very similar to that of other quaternary substituent-bearing carbons.

<sup>13</sup>C Chemical shifts for 4-substituted tricyclenes (1)–(10) are given in Table 1 and the corresponding substituent induced chemical shift increments are given in Table 2. We have also determined the <sup>13</sup>C chemical

TABLE 1

<sup>13</sup>C Chemical shifts (p.p.m.) of 4-substituted tricyclenes

Substituent	C(1)	C(2), C(6)	C(3), C(5)	C(4)	C(7)	C(8), C(9)	C(10)	C(11)	C(12)
H	26.3	20.6	31.3	41.8	43.1	19.4	9.4		
Me	28.8	20.3	38.2	43.3	44.2	17.7	11.5	12.2	
CH <sub>2</sub> OH	29.1	19.9	33.8	49.0	44.2	18.5	10.7	67.7	
OH	29.8	19.2	36.1	79.9	43.1	17.3	12.2		
CO <sub>2</sub> H	28.0	19.6	35.1	52.8	46.9	18.7	10.7		
CO <sub>2</sub> Me	27.8	19.5	34.9	52.8	46.7	18.7	10.7	173.8	51.0
COMe	28.1	19.6	35.1	60.4	46.9	18.8	10.5	210.3	29.7
Cl	27.5	19.3	39.3	69.5	45.8	17.6	12.1		
NO <sub>2</sub>	28.0	18.8	35.2	89.7	47.7	17.8	11.2		
NH <sub>2</sub>	28.7	19.9	37.9	60.6	43.8	17.2	12.3		

The <sup>13</sup>C n.m.r. spectrum of nortricyclene has been reported by Roberts and his co-workers;<sup>4</sup> since nortricyclene possesses C<sub>3v</sub> symmetry, only three signals were observed, C(1), C(2), and C(6) absorbing at 10.2 p.p.m. from tetramethylsilane, C(3), C(5), and C(7) at 33.5, and C(4) at 30.0 p.p.m. These values were subsequently confirmed and extended to include a number of methylated nortricyclenes.<sup>5</sup>

<sup>3</sup> J. F. Chiang, C. F. Wilcox, and S. H. Bauer, *Tetrahedron*, 1969, **25**, 369.

<sup>4</sup> J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 7107.

<sup>5</sup> E. Lippmaa, T. Pehk, and J. Paasivirta, *Org. Magnetic Resonance*, 1973, **6**, 277.

shifts for three 1-substituted bicyclo[2.2.2]octanes (13)–(15) which supplement the existing published values.<sup>2</sup> These data are presented in Table 3.

C(4) Chemical shifts of tricyclenes (1)–(10) show, empirically, a good linear correlation with the electronegativity parameter  $E_R$ <sup>7</sup> (correlation coefficient 0.988). A similar though less exact correlation has been noted

<sup>6</sup> (a) A. Saika and C. P. Slichter, *J. Chem. Phys.*, 1954, **22**, 56; (b) D. M. Grant and B. V. Cheney, *J. Amer. Chem. Soc.*, 1967, **89**, 5315.

<sup>7</sup> J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, 1961, **34**, 1099. Values of  $E_R$  for hydroxy and nitro-substituents are taken from D. J. Sardella, *J. Mol. Spectroscopy*, 1969, **31**, 70; P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1963, **85**, 2709.

for adamantanes<sup>1</sup> (II) and cyclohexyl derivatives.<sup>8</sup> Thus the  $\alpha$ -shift parameters of substituted hydrocarbons are generally inductive in origin.<sup>9</sup> Substituent induced

TABLE 2

<sup>13</sup>C Chemical shift increments (p.p.m.) of 4-substituted tricyclenes

Substituent	C(1)	C(2), C(6)	C(3), C(5)	C(4)	C(7)	C(8), C(9)	C(10)
H	0	0	0	0	0	0	0
Me	2.5	-0.3	6.9	1.5	1.1	-1.7	2.1
CH <sub>2</sub> OH	2.8	-0.7	2.5	7.2	1.1	-0.9	1.3
OH	3.5	-1.4	4.8	38.1	0.1	-2.1	2.8
CO <sub>2</sub> H	1.7	-1.0	3.8	11.0	3.8	-0.7	1.3
CO <sub>2</sub> Me	1.5	-1.1	3.6	11.0	3.6	-0.7	1.3
COMe	1.8	-1.0	3.8	18.6	3.8	-0.6	1.1
Cl	1.2	-1.3	8.0	27.7	2.7	-1.8	2.7
NO <sub>2</sub>	1.7	-1.8	3.9	47.9	4.6	-1.5	1.8
NH <sub>2</sub>	2.4	-0.7	6.6	18.8	0.7	-2.2	2.9

Positive values in this and other Tables of shift increments indicate shift to low field.

TABLE 3

<sup>13</sup>C Chemical shifts (p.p.m.) of 1-substituted bicyclo[2.2.2]octanes

Substituent	C(1)	C(2)	C(3)	C(4)	C(9)
OH	69.09	33.91	27.20	24.41	
CH <sub>2</sub> OH	32.44	27.78	25.77	24.68	71.92
CO <sub>2</sub> H	38.17	27.94	25.35	23.73	185.2

chemical shift increments,  $\alpha$ -shifts, in tricyclenes are generally within 1 p.p.m. of the corresponding values in adamantanes (II) except in the case of chloro- and nitro-derivatives where the tricyclene values are appreciably smaller. From values of low-field  $\alpha$ -shifts in the t-butyl group and three related ring systems in Table 4, it is seen that  $\alpha$ -shifts are greatest for 1-substituted bicyclo[2.2.2]octanes whereas tricyclenes give amongst the smallest shifts which may exceed those of adamantanes for certain substituents. Lippmaa's group<sup>10</sup> has shown that in a number of bicyclic systems both the

effect is responsible in part for the  $\alpha$ -shift sequence observed in the four systems for which data are given in Table 4.

In tricyclenes (1)–(10) both the equivalent C(3) and C(5) secondary carbons and the C(7) quaternary carbon

TABLE 4

$\alpha$ -Carbon <sup>13</sup>C chemical shift increments (p.p.m.)

	Substituent						
	H	Me	CH <sub>2</sub> OH	OH	CO <sub>2</sub> H	Cl	NO <sub>2</sub>
t-Butyl	0	2.7	7.7	4.35	13.5	40.1	60.0
Bicyclo[2.2.2]oct-1-yl	0		7.75	44.4	14.5	42.3	
Adamantan-1-yl	0	1.3	6.1	38.9	11.8	38.6	55.7
4-Tricycyl	0	1.45	7.2	38.1	11.0	27.7	47.9

are  $\beta$  to the substituent. Although the present data are less extensive than those for adamantanes (II) we also find that Class I substituents<sup>1</sup> which contain not more than one atom heavier than hydrogen bring about larger low-field shifts of the secondary  $\beta$ -carbons C(3) and C(5) in tricyclenes (1)–(10). For those substituents which possess more than one atom heavier than hydrogen (Class II) the low-field  $\beta$ -shifts are consistently greater for C(3) and C(5) in the 4-substituted tricyclenes than for  $\beta$ -carbons of adamantanes (II). Table 5 gives the  $\beta$ -carbon chemical shifts for four structural types together with the derived low-field  $\beta$ -shifts.

4-Substituted tricyclenes may be conceptually derived from bridgehead substituted adamantanes (II) by (i) deletion of the marked carbons in (II) and replacement by bridgehead-bridgehead bonds, (ii) introduction of three methyl groups. The effect of this process is to introduce into (nor)tricyclene significant strain and in particular distortion of bond angles.<sup>3</sup> In the case of 1-nitroadamantane it is calculated, with the aid of standard nitro-parameters,<sup>11</sup> that in the eclipsed conformation with an O(1)–N–C(1)–C(2) dihedral angle

TABLE 5

$\beta$ -Carbon <sup>13</sup>C chemical shifts and substituent increments (p.p.m.)

	Substituent						
	H	Me	Cl	OH	CH <sub>2</sub> OH	CO <sub>2</sub> H	NO <sub>2</sub>
t-Butyl	24.3	31.5	33.6	31.6	26.6	26.3	26.9
C(1)	0	7.2	9.3	7.3	2.3	2.0	2.6
Bicyclo[2.2.2]oct-1-yl	26.81		36.95	33.91	27.78	27.90	
C(2)	0		10.14	7.10	0.97	1.1	
Adamantan-1-yl	38.0	44.6	48.0	45.8	39.4	38.7	40.8
C(2)	0	6.6	10.0	7.8	1.4	0.7	2.8
4-Tricycyl	31.3	38.2	39.3	36.1	33.8	35.1	35.2
C(3), C(5)	0	6.9	8.0	4.8	2.5	3.8	3.9

bridgehead methyl induced  $\alpha$ -shift and  $J_{C(1)-H}$  (in the unsubstituted hydrocarbon) correlate linearly with the <sup>13</sup>C chemical shift of the methyl carbon and the authors suggested that these effects are related to hybridisation of the bridgehead carbon. It is possible that such an

equal to 0°, that the C(1)···C(2) non-bonded distance is 2.62 Å. Similarly for 4-nitrotricyclene, taking  $\theta = 115.3^\circ$  the C(1)···C(3) non-bonded distance in the conformation with dihedral angle O(1)–N–C(4)–C(3) = 0° is 2.74 Å. In conformations in which the above dihedral angles depart from 0° to the same extent, the

<sup>8</sup> T. Pehk and E. Lippmaa, *Org. Magnetic Resonance*, 1971, **3**, 679.

<sup>9</sup> W. J. Horsley and H. Sternlicht, *J. Amer. Chem. Soc.*, 1968, **90**, 3738.

<sup>10</sup> T. Pehk, M. Alla, and E. Lippmaa, *Org. Magnetic Resonance*, 1973, **5**, 351.

<sup>11</sup> Chemical Society Special Publication No. 18, 1965.

O(1)-C(3) distance in 4-nitrotricyclene will always be greater than the corresponding O(1)-C(2) distance in 1-nitroadamantane. The diamagnetic screening by the nitro-oxygen atoms on C(2) of 1-nitroadamantane therefore has to act over a shorter distance as compared with C(3) of 4-nitrotricyclene; accordingly the contribution of this component to the  $\beta$ -shifts is greater in the adamantanes and the greater downfield  $\beta$ -shift for C(3) in 4-nitrotricyclene (9) with respect to the C(2)  $\beta$ -shift in 1-nitroadamantane is rationalised. Similar conclusions are in order for other Class II bridgehead substituents. Analogous geometric considerations of 1-substituted bicyclo[2.2.2]octanes with Class II substituents accord with comparable values of  $\beta$ -shifts to those of the corresponding 1-substituted adamantanes. In general Class I substituents bring about rather smaller low-field  $\beta$ -shifts at C(3) and C(5) of the tricyclenes than those of other systems in Table 5. In *endo*- and *exo*-2-substituted norbornanes, larger  $\beta$ -shifts are found for both C(3) and C(1) for Class I substituents, although for the latter carbon the contrast with Class II substituents is less marked.<sup>4</sup>

The response of the low-field  $\beta$ -shifts for the quaternary C(7) to substituent variation is different from that of C(3) and C(5). The effect of *gem*-dimethyl substitution at C(7) is two fold: (i) a significant reduction of C(7)  $\beta$ -shifts occurs with respect to those of C(3) and C(5) when the substituent belongs to Class I (a similar effect has been alluded to previously) and (ii) relatively little change is noted for the corresponding  $\beta$ -shifts with Class II substituents.

Bicyclo[2.2.2]octanes (16) and (13) provide a further example of the diamagnetic shielding component exerted at  $\beta$ -carbons by Class II substituents. In these molecules the bridgehead substituents possess rather similar electronic character and the hydroxy-induced  $\beta$  shift of 7.1 p.p.m. in (13) compares with a corresponding methoxy-value of 3.25 p.p.m. in (16). The larger  $\beta$ -shift in (16) with respect to the value of 0.97 p.p.m. for the isomeric hydroxymethyl derivative (14) is difficult to rationalise, particularly as the relative shielding capacities of methyl in (16) and hydroxy in (14) are unknown.

The nature of the tricyclo[2.2.1.0<sup>2,6</sup>] ring skeleton in tricyclenes (1)–(10) militates against any direct 1,4-shielding interaction with the ring carbons C(1), C(2), and C(6). The observed  $\gamma$ -shifts for the equivalent cyclopropane carbons C(2) and C(6) are such that more strongly electron-withdrawing substituents absorb at higher field and empirically a good correlation holds for C(2) and C(6) chemical shifts and  $E_R$ . Response of the C(2) and C(6) shifts to substituent variation differs from that of  $\gamma$ -carbons in adamantanes (11) which are to low field. The possibility was mentioned<sup>1</sup> of an ill understood steric influence of substituents on  $\gamma$ -carbons in adamantanes (11) together with associated small changes in molecular geometry; however in the tricyclenes skeletal deformation is considered much less likely. Hybridisation differences<sup>12</sup> of the  $\gamma$ -carbons may be

among the factors which produce different  $\gamma$ -shifts in the two series. By way of contrast  $\gamma$ -shifts of the quaternary cyclopropane C(1) in tricyclenes (1)–(10) are to low field.

The  $\gamma$ -shifts for tertiary and secondary  $\gamma$ -carbons of 1-substituted adamantanes and bicyclo[2.2.2]octanes respectively are given in Table 6. Although no formal

TABLE 6

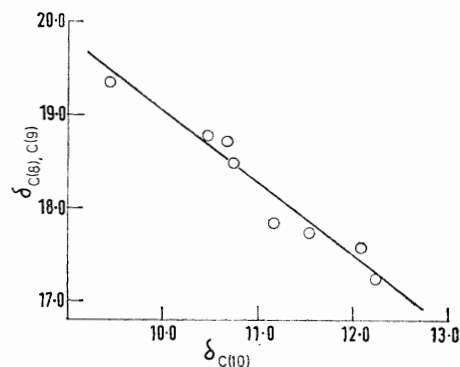
Bridgehead substituent induced  $\gamma$ -shifts (p.p.m.) for C(3) in 1-substituted bicyclo[2.2.2]octanes and  $\gamma$ -carbons in bridgehead substituted adamantanes

X	C(3)	$\gamma$ -C
OH	0.39	2.3
OMe	0.89	
F	1.27	3.2
Cl	2.14	3.1
Br	3.03	3.9
CH <sub>2</sub> OH	-1.04	-0.2
CO <sub>2</sub> H	-1.46	-0.6

$\gamma$ -Shifts for C(3), C(5), and C(4) in tricyclenes (1)–(9) are given in Table 2.

correlation exists between the two series, the  $\gamma$ -carbons appear to respond in a broadly similar manner;  $\gamma$ -shifts are consistently under a greater diamagnetic influence in the bicyclo[2.2.2]octanes. It appears that the correspondence between C(2) and C(3) chemical shifts noted for 1-substituted bicyclo[2.2.2]octanes<sup>2</sup> becomes less exact as the range of substituent data increases. Presently however differences in  $\gamma$ -shifts of ring carbons in bridgehead substituted fused ring systems cannot be adequately rationalised and the values themselves are of little predictive value.

Tricyclenes (1)–(10) give rise to two absorptions which are attributable to exocyclic methyl carbons with



<sup>13</sup>C Chemical shifts (p.p.m.) of C(8) and C(9) versus C(10) in 4-substituted tricyclenes

the more intense C(8) and C(9) absorptions downfield from those of C(10). Interestingly the high-field  $\gamma$ -shifts for C(8) and C(9) correlate with the corresponding low-field  $\delta$ -shifts exhibited by C(10) (Figure) (correlation coefficient 0.970). It is noted that magnitudes of the C(10)  $\delta$ -shifts are greater than those of the corresponding

<sup>12</sup> W. A. Bennett, *J. Chem. Educ.*, 1967, **44**, 17.

C(8) and C(9)  $\gamma$ -shifts. Thus an amplification of the common substituent effects which are controlling, at least in part, the chemical shifts of C(8)—(10) occurs in the case of C(10) and is mediated by the cyclopropane ring. Since in the tricyclenes (1)—(10) there is no direct interaction between the C(4) substituent and the C(10) methyls the correlation between C(8) and C(9)  $\gamma$ -shifts and C(10)  $\delta$ -shifts renders unlikely any significant direct interaction between the C(4) substituent and the C(8) and C(9) methyl groups. The greater magnitude of the C(10)  $\delta$ -shifts as compared with the C(8) and C(9)  $\gamma$ -shifts is contrary to expectations based on a field effect of the substituent.

A significant amount of  $^{13}\text{C}$  chemical shift data has been assimilated for mono- and bi-cyclic compounds with two methyl substituents. From a collation of such data<sup>13</sup> it has been shown that a methyl group in methylcyclohexane experiences a low-field  $\beta$ -shift of 8.7 p.p.m. on introduction of a further methyl group to give 1,1-dimethylcyclohexane. Analogously high-field  $\gamma$ -shifts of 4.4 and 2.5 p.p.m. respectively are observed for *cis*- and *trans*-1,2-dimethylcyclohexanes whereas low-field  $\delta$ -shifts of *ca.* 0.5 p.p.m. are found for *cis*- and *trans*-1,3-dimethylcyclohexanes. Examination of  $^{13}\text{C}$  chemical shift data of a number of methylnorbornanes and methylnorbornenes<sup>14</sup> indicates that here too methyl shifts of alternating sign and diminishing magnitude are consistently observed as a further methyl is introduced  $\beta$ ,  $\gamma$ , or  $\delta$  to the original methyl. Although the possibility of ring distortion cannot be excluded as a contributory source of the methyl shifts, it is noted that  $\gamma$ -shifts derived for *endo*-2-*exo*-3-dimethylnorbornanes, a substituent pattern which gives rise to the largest distortions,<sup>15</sup> do not appear atypical. The different senses of the C(10) and C(8) and C(9) methyl shifts observed throughout the tricyclenes (1)—(10) with a wide range of substituent character thus appear to extend the relationship noted previously.

Additionally certain of Lippmaa's  $^{13}\text{C}$  chemical shift data for nortricyclene derivatives<sup>5</sup> are worthy of consideration. In 1-methylnortricyclene (17), C(8) absorbs at 15.9 p.p.m. and in (2), C(10) absorbs at 11.1 p.p.m. [since both determinations were performed in the same laboratory we have used the shift data of Lippmaa<sup>5</sup> which for the methyl carbons of (2) differ by >1 p.p.m. from the present results (Table I); our numbering of the exocyclic methyl groups also differs]. Thus introduction of two equivalent methyl groups at C(7) in (17) results in a  $\gamma$ -shift of -4.8 p.p.m. 1-Methylnortricyclene (17) may also be compared with cyclofenchene (18), where the *gem*-dimethyls although formally non-equivalent both absorb<sup>5</sup> at 20.3 p.p.m. In (18), the C(10) methyl now absorbs at 16.8 p.p.m. and with respect to C(8) in (17) has undergone a low-field  $\delta$ -shift

of 0.9 p.p.m. This result is now in accord with the general pattern outlined above and it is not necessary to invoke changes in geometry in the rigid nortricyclene ring skeleton.<sup>5</sup>

Support for the existence of charge alternation within the cyclic frameworks of 1-methylcyclohexane<sup>16</sup> and 1-chloroadamantane<sup>17</sup> has been provided by charge density calculations (see also refs. 18 and 19) and this finding was postulated as the basis for high-field  $\delta$ -effects in monosubstituted cyclohexanes<sup>8</sup> and 1-substituted adamantanes.<sup>1</sup> Charge alternation in tricyclenes (1)—(10) is worthy of consideration as a contributing factor in bringing about the related high-field C(8) and C(9)  $\gamma$ -shifts and low-field C(10)  $\delta$ -shifts. However CNDO charge density calculations on (1), (2), and (8) do not provide conclusive evidence for such a mechanism. Recently Lippmaa's group<sup>5</sup> has collated factors which affect  $\gamma$ -shifts and has indicated the complex nature of the problem of understanding these shifts which is hindered by the absence, *inter alia*, of suitable u.v. spectral data. Within the tricyclene series (1)—(10) the individual dependence with substituent character of the chemical shifts of the three  $\gamma$ -carbon types, C(1); C(2) and C(6); C(8) and C(9), where no direct interaction with substituent occurs, illustrates this point and implies that for predictive purposes the character of the carbon must be taken into account.

A comparison with the previously obtained results of Olah's group<sup>20</sup> shows that the chlorine induced  $\alpha$ -,  $\beta$ -, and  $\gamma$ -shifts for 4-substituted nortricyclonium ions are of similar magnitude to those of the C(4); C(3) and C(5); and C(2) and C(6) shifts obtained from (8) and (1) with the reservation that the  $\gamma$ -shifts are in opposite senses.

Parenthetically we note that the  $^1\text{H}$  n.m.r. absorptions for the cyclopropyl methine protons of tricyclenes (1)—(10) and to a lesser extent the C(10) methyl protons undergo shift to low field (see Experimental and ref. 20) with increasing electron-withdrawing character of the C(4) substituent.

#### EXPERIMENTAL

$^1\text{H}$  N.m.r. spectra were recorded on a Varian HA 100 (100 MHz) spectrometer with tetramethylsilane as an internal standard. Mass spectra were determined on an A.E.I.—G.E.C. MS12 spectrometer. M.p.s were recorded on a Kofler hot-stage apparatus, unless otherwise stated, and are uncorrected. Microanalytical determinations were carried out by the Microanalytical Department, University of Glasgow.  $^{13}\text{C}$  N.m.r. spectra were obtained on a Bruker HFX 13 spectrometer operating in the Fourier transform mode at 22.63 MHz and are quoted relative to internal tetramethylsilane as standard. Proton noise decoupling

<sup>17</sup> H. Fujimoto, Y. Kitagawa, H. Hao, and H. Fukui, *Bull. Chem. Soc. Japan*, 1970, **43**, 52.

<sup>18</sup> J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, 1967, **89**, 4253.

<sup>19</sup> D. J. Sardella, *J. Amer. Chem. Soc.*, 1973, **95**, 3809.

<sup>20</sup> G. A. Olah, P. R. Clifford, and C. L. Jeuell, *J. Amer. Chem. Soc.*, 1970, **92**, 5531.

<sup>13</sup> J. Mason, *J. Chem. Soc. (A)*, 1971, 1038.

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was performed by means of a 90 MHz broad band decoupler. Probe temperature was 35°. Chemical shifts are accurate to 0.1 p.p.m. <sup>13</sup>C Spectra of (13) and (14) were run on a Varian XL 100 spectrometer. The Bruker and Varian spectra were recorded respectively at Queen Mary College, London, and the University of Edinburgh under the S.R.C. Fourier Transform Service.

Solvents were AnalaR grade. Organic solutions were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Compounds (4), (5), (7),<sup>21</sup> (14), and (15)<sup>22</sup> have been described previously.

**4-Hydroxymethyltricyclene (3).**—A solution of tricyclene-4-carboxylic acid<sup>21</sup> (5) (300 mg, 1.67 mmol) and lithium aluminium hydride (*ca.* 100 mg) in anhydrous ether was refluxed overnight. Excess of hydride was destroyed by cautious addition of a freshly made up aqueous solution of anhydrous sodium sulphate. The solution was then filtered and the precipitate was washed thoroughly with ether. Ether was removed to give (3) (251 mg, 91%) as a solid. Recrystallisation from the minimum volume of light petroleum (b.p. 60–80°) gave an analytical *sample*, m.p. 141–142°,  $\delta$  (CDCl<sub>3</sub>) 0.80 (6H, s), 0.91 (2H, s), 1.03 (3H, s), 1.59 (2H) and 1.20 (2H) (AB,  $J_{AB}$  10.0 Hz), 1.32br (1H, s, exchangeable with D<sub>2</sub>O), and 3.72 (2H, s) (Found: C, 79.3; H, 10.75. C<sub>11</sub>H<sub>18</sub>O requires C, 79.45; H, 10.9%).

**4-Methyltricyclene (2).**—To a solution of 4-hydroxymethyltricyclene (3) (400 mg, 2.41 mmol) in anhydrous pyridine (8 ml) at 0° was added toluene-*p*-sulphonyl chloride (476 mg, 2.5 mmol). The solution was stirred for two days and then poured into ice-water; 2*N*-hydrochloric acid was added with rapid stirring until the solution attained pH 2. After extraction (3 × 100 ml) with pentane-ether (30 : 70), the combined extracts were washed with sodium hydrogen carbonate solution; solvent was removed to give 4-*p*-tolylsulphonyloxymethyltricyclene (755 mg).

An ethereal solution of the sulphonate and lithium aluminium hydride (*ca.* 200 mg) was refluxed overnight. The reaction mixture was worked up as for (3) except that ether was removed at *ca.* 10°. Crude (2) (310 mg), obtained as a waxy off-white solid, was chromatographed on alumina (Woelm neutral, grade 3); elution with *n*-pentane gave pure 4-methyltricyclene [240 mg, 66.3% from (3)] as a waxy solid, m.p. 110–111° (sealed capillary),  $\delta$  (CDCl<sub>3</sub>) 0.70 (6H, s), 0.82 (2H, s), 0.89 (3H, s), and 1.04 (3H, s), and 1.45 and 1.55 [A part of an AB pattern (the B part of this pattern was obscured by the methyl absorptions)  $J_{AB}$  10.0 Hz]. It was not possible to obtain a satisfactory microanalysis for (3), presumably on account of its volatility (Found: C, 85.65; H, 11.8%;  $M^+$ , 150. C<sub>11</sub>H<sub>18</sub> requires C, 88.0; H, 12.0%;  $M$ , 150).

**Methyl Tricyclene-4-carboxylate (6).**—A solution of (5) in ether was methylated with diazomethane in the usual way. The ester was obtained as a sweet smelling oil which on prolonged standing crystallised to a low melting solid,  $\delta$  (CDCl<sub>3</sub>) 0.90 (6H, s), 0.95 (2H, s), 1.04 (3H, s), 2.01 (2H) and 1.43 (2H) (AB,  $J_{AB}$  10.0 Hz), and 3.66 (3H, s).

**4-Nitroisoborneol.**—1-Nitrocamphene<sup>23</sup> (15 g, 0.083 mol) and trichloroacetic acid (65 g, 0.4 mol) were placed in a 500 ml round bottomed flask. The solution which formed on warming was stirred at 100° for 15 h after which 1-nitrocamphene had been consumed (*i.r.*). The flask was then cooled in ice and partial neutralisation was effected by

cautious addition of a solution of sodium hydroxide (13.2 g) in water (300 ml). The resulting solution was then extracted with ether and the ether layer washed with sodium hydrogen carbonate until neutral. Removal of ether on a rotary evaporator gave 4-nitroisobornyl trichloroacetate (26.5 g) as an oil,  $\nu_{max}$  (film) 1760, 1535, 1380, and 1245 cm<sup>-1</sup>.

To 4-nitroisobornyl trichloroacetate (13 g) in water (80 ml) was added potassium hydroxide (6.4 g). The mixture was refluxed for 2 h, a small amount of ethanol being added to the hot solution to effect homogeneity. After cooling the solution was extracted into ether and removal of ether gave 4-nitroisoborneol (6.2 g, 83%). Recrystallisation from ethanol gave m.p. 266–267° (sealed capillary),  $\nu_{max}$  (Nujol) 3430br, 1540, and 1395–1370 cm<sup>-1</sup>,  $\delta$  (CDCl<sub>3</sub>; Varian T60) 3.67–3.99 (*endo*-3-H) (Found: C, 60.1; H, 8.4; N, 6.4. C<sub>10</sub>H<sub>17</sub>NO<sub>3</sub> requires C, 60.3; H, 8.6; N, 7.05%).

**4-Nitrocaphor.**—4-Nitroisoborneol (12.0 g, 0.65 mol) was dissolved in acetone (140 ml), cooled to 0°, and stirred vigorously with a magnetic stirrer. To the solution Jones reagent (20 ml) was added dropwise over 5 min; after a further 5 min the mixture was washed with water (300 ml). The aqueous layer was extracted with ether (3 × 80 ml), and ether was removed to give a solid which was recrystallised from ethyl acetate-light petroleum (b.p. 60–80°) to give 4-nitrocaphor (10.8 g, 90%), m.p. 220–221°,  $\delta$  (CDCl<sub>3</sub>) 0.95 (3H, s), 1.00 (3H, s), 1.12 (3H, s), and 3.26 (*exo*-3-H) and 2.55 (*endo*-3-H) (AB,  $J_{AB}$  18.0 Hz) (low-field component, *exo*-3-H, further split by coupling with *exo*-5-H,  $J$  3.85 Hz) (Found: C, 60.8; H, 7.65; N, 7.2. C<sub>10</sub>H<sub>15</sub>NO<sub>3</sub> requires C, 60.9; H, 7.65; N, 7.1%).

**Camphor *p*-Tolylsulphonylhydrazones.**—Camphor derivatives (*ca.* 10 g) and an equimolar amount of *p*-tolylsulphonylhydrazine were dissolved in the minimum amount of warm ethanol and concentrated hydrochloric acid (4 drops) was added. The solution was refluxed for 30 min; on cooling, crystals separated. These were filtered and recrystallised from ethanol to give the *p*-tolylsulphonylhydrazones in >85% yield: camphor *p*-tolylsulphonylhydrazone, m.p. 163–164° (lit.,<sup>24</sup> 163–164°): 4-chloro-camphor *p*-tolylsulphonylhydrazone, m.p. 197–198° (Found: C, 57.8; H, 6.7; N, 7.95. C<sub>17</sub>H<sub>23</sub>ClN<sub>2</sub>O<sub>2</sub>S requires C, 57.55; H, 6.55; N, 7.9%); 4-nitrocaphor *p*-tolylsulphonylhydrazone, m.p. 210° (Found: C, 56.0; H, 6.35; N, 11.5. C<sub>17</sub>H<sub>23</sub>N<sub>3</sub>O<sub>4</sub>S requires C, 55.9; H, 6.35; N, 11.5%).

**Tricyclenes.**—Into a three necked 250 ml round bottomed flask were placed the camphor *p*-tolylsulphonylhydrazone (14.8 mmol) and dry tetrahydrofuran (80 ml). The stirred slurry was maintained under dry nitrogen and a solution of methyl-lithium in hexane (Lithium Corporation of America; 7 ml of a 2.1*M* solution, 14.2 mmol) was injected through a serum cap. The temperature was kept at 0–5° during addition and for 30 min thereafter. After 30 min at room temperature the solvent was removed at 40°. The resulting salt was hydrolysed at 200° and the tricyclene was swept into a dry-ice trap by the nitrogen stream with warming of the tube from the reaction flask to the dry-ice trap. Tricyclenes were removed from the trap with pentane which was removed at 10°. Small amounts of olefinic material in tricyclene and 4-chlorotricyclene (*n.m.r.*) was removed by chromatography on a silver nitrate-alumina (Woelm

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<sup>23</sup> Y. Brunel, H. Lemaire, and A. Rassat, *Bull. Soc. chim. France*, 1964, 1895.

<sup>24</sup> W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 1952, 4735.

neutral, grade 3) column.<sup>25</sup> Tricyclenes were preferentially eluted with pentane. 4-Nitrotricyclene was purified by recrystallisation from ethanol. Tricyclene had  $\delta$  (CDCl<sub>3</sub>) 0.82 (8H, s, 2 × CH<sub>3</sub> and cyclopropyl protons), 1.01 (3H, s), 1.66 (2H) and 1.03 (2H) (AB,  $J_{AB}$  10.4 Hz), and 1.40 (1H, s). The absorptions for the AB pattern and the bridgehead C(4) proton were broad. 4-Chlorotricyclene had  $\delta$  (CDCl<sub>3</sub>) 0.86 (6H, s), 0.98 (2H, s), 1.08 (3H, s), 1.95 (2H) and 1.56 (2H) (AB,  $J_{AB}$  10.1 Hz). It was not possible to obtain a satisfactory microanalysis for this material because of its volatility (Found: C, 69.1; H, 9.0%;  $M^+$ , 170, 172. C<sub>10</sub>H<sub>15</sub>Cl requires C, 70.75; H, 8.85%;  $M$ , 170, 172). 4-Nitrotricyclene had m.p. 135–136°,  $\delta$  (CDCl<sub>3</sub>)

0.99 (6H, s), 1.09 (3H, s), 1.12 (2H, s), and 2.40 (2H) and 1.85 (2H) (AB,  $J_{AB}$  10.6 Hz) (Found: C, 66.15; H, 8.45; N, 7.8. C<sub>10</sub>H<sub>15</sub>NO<sub>2</sub> requires C, 66.25; H, 8.35; N, 7.75%).

4-Aminotricyclene was prepared by treatment of an ethereal solution of 4-nitrotricyclene (2.3 g) with lithium aluminium hydride in the usual way to give 4-aminotricyclene (1.25 g, 65%) as an unpleasant smelling waxy solid,  $\delta$  (CCl<sub>4</sub>) 0.73 (6H, s), 0.85 (2H, s), 1.03 (3H, s), and 1.58 (2H) and 1.23 (2H) (AB,  $J_{AB}$  10.1 Hz).

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