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Fluorine Deshielding in the Proximity of a Methyl Group. An Experimental and Theoretical Study

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^{19}F chemical shifts are reported for a series of alkyl-substituted fluoronaphthalenes and related compounds that exhibit steric crowding around the fluorine atom due to the proximity of methyl groups. Comparisons of these chemical shifts with others measured in similar compounds but without the corresponding methyl groups show that this crowding effect produces a large low-field shift of the ^{19}F signal. Similar effects, but with an even larger sensitivity to the steric crowding, were recently reported for ^{17}O chemical shifts. The electronic origin for this proximity effect on ^{19}F chemical shifts is analyzed within the molecular orbital theory, at the INDO level, using the inner projections of the polarization propagator technique. It is found that the presence of the methyl group produces an increase in the absolute value of the paramagnetic term of the magnetic shielding constant.

KEY WORDS ^{19}F NMR 1-Alkyl-8-fluoronaphthalenes Fluorine deshielding ^{19}F chemical shift theory Magnetic shielding tensor calculations

INTRODUCTION

The dependence of chemical shifts of various nuclei on proximity effects has attracted much attention.[1] An interesting description of such effects was reported a few years ago by Li and Chesnut[2] when they correlated the so-called beta- and gamma-effects on chemical shifts with van der Waals interactions, as calculated by the Allinger force field method.[3] They concluded that the attractive van der Waals interaction produces a shielding effect while the repulsive van der Waals interaction yields a large deshielding effect, regardless of the nucleus considered. In a subsequent paper, Li and Chesnut[4] mainly ascribed the deshielding effect to an increase in $1/r^3$ owing to the contraction of the orbitals involved in the repulsive interaction. Such an increase corresponds to a larger paramagnetic contribution, which, being negative, yields a deshielding effect.

Recently, Boykin and co-workers measured the ^{17}O chemical shifts of a series of alkyl-substituted indanones[5] and alkyl-substituted 1-tetralones[6] where the carbonyl oxygen shows different degrees of steric crowding with methyl groups. Large deshielding of the ^{17}O nucleus is observed. For instance, a *tert*-butyl group placed in a *peri* position to the carbonyl ^{17}O nucleus in indanones induces a deshielding of 36 ppm.[5] The high sensitivity of the deshielding effect to the distance between the *tert*-butyl and the carbonyl groups is apparent when the value is compared with the deshielding effect of about 50 ppm observed by the same authors for 1-*tert*-butylanthraquinone.[7]

Since a similar deshielding effect to that observed on ^{17}O chemical shifts by Boykin and co-workers can be expected for ^{19}F chemical shifts, we have undertaken a study of the effect of steric crowding between a methyl group and a fluorine atom in several fluoronaphthalene derivatives and related compounds as measured by NMR spectroscopy. Although the ^{19}F NMR spectra show a strong fluorine deshielding effect which increases as the distance between the methyl group and the fluorine atom decreases, the sensitivity of the ^{19}F chemical shifts to such an effect is found to be smaller than that of ^{17}O chemical shifts. The largest effect is observed in 1-*tert*-butyl-8-fluoronaphthalene, in which the fluorine atom is deshielded by 27.5 ppm with respect to that of 1-fluoronaphthalene.

To achieve a deeper insight into this problem than can be obtained from the correlation between the deshielding effect and the van der Waals interactions, as calculated by the Allinger force field method,[3] we have applied the IPPP technique[8] (inner projections of the polarization propagator). This technique provides an estimate of the contributions to a second-order property originated in a given molecular fragment[9] and, therefore, is particularly well suited to analyze proximity effects. This analysis consists mainly of the following three steps: (i) the ground-state wave function of the molecule under study is calculated; (ii) a localization procedure is applied to separate the molecular fragments; and (iii) the desired second-order property is calculated using the polarization propagator approach. The polarization propagator is inner projected onto the molecular fragment whose local contribution is sought.

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Each of these three steps can be carried out using different approaches, with different degrees of approximation. With regard to step (i), it is well known that, in general, the accurate calculation of the magnetic shielding tensor is a difficult task for molecular orbital theory. Recently, the IGLO[10] and LORG[11] approaches have been used. Fluorine magnetic shielding tensors require, in general, more extended basis sets than, for example, carbon magnetic shielding tensors.[12] Therefore, for an accurate analysis of all of the factors defining fluorine chemical shifts in medium sized molecules, rather large computational requirements exist. However, as discussed previously,[13] components which originate in some electronic mechanisms can be adequately described with a wavefunction of modest quality. As several electronic mechanisms can be discriminated with the IPPP technique,[8] this approach can be applied successfully to problems where such mechanisms are dominant. The very good correlations obtained by Li and Chesnut[2,4] and by Boykin and co-workers[5,6] between the deshielding effect and the van der Waals interaction between an oxygen atom and a close methyl group, when a method so simple as the force field approach[3] is applied, indicates on the one hand that it is a proximate effect and on the other that it would not require a good-quality ground-state wavefunction to be properly described. In this paper the ground-state wavefunctions are calculated at the standard[14] INDO approximation.[15] Being a proximity effect, contributions to the magnetic shielding constant originated only on the C—F and on the proximate X groups are calculated. Such contributions will hereafter be referred to as 'local contributions'. Very good agreement between experimental and theoretical deshielding values in two model compounds is obtained. Owing to such good agreement, the localization procedure in the IPPP approach[8] is repeatedly applied to the molecular fragments until local components are expressed in terms of contributions of bonds, electron lone pairs, and antibonding orbitals in the same fashion as applied previously[16,17] to the study of coupling constants.

EXPERIMENTAL SECTION

Synthesis of compounds

Procedures for the preparation of the following compounds have been published previously: **1**,[18] **2**,[18] **11**,[19a] **12**,[19b] **13**,[19c] **14**,[19b] **15**,[19c] **16**,[19a] **17**[18] and **18**.[18] Although we have previously presented the syntheses of **4**, **5**, **9** and **10**,[19d] full experimental details have not been previously reported. The general procedure for the syntheses of **4–10** (see below) involves the Diels–Alder cycloaddition of an aryne and a 2-substituted furan. The resulting naphthalen-1,4-endoxide is catalytically hydrogenated and then dehydrated with acid to afford the desired naphthalene. Compound **3** is commercially available.

2-*tert*-Butylfuran. This was prepared according to the method of Fitzpatrick *et al.*[20] A magnetically stirred solution of 2-furoic acid (98%, 69.9 g, 0.611 mol) in CH_2Cl_2 (650 ml) at 5 °C was treated with $AlCl_3$ (167 g, 1.25 mol) in seven portions. The $AlCl_3$ was added slowly so as to keep the internal temperature below 10 °C. After addition was complete, *tert*-butyl chloride (58 g, 0.63 mol) was added dropwise over 30 min keeping the internal temperature below 10 °C. The mixture was allowed to warm to room temperature and stirred for 2 h. The mixture was then poured over ice (500 g), the layers were separated and the aqueous layer was further extracted with fresh CH_2Cl_2 (4 × 200 ml). The combined organic extracts were washed with water (500 ml) and brine (500 ml) and were concentrated *in vacuo* to give a yellow residue that began to crystallize. The residue was treated with quinoline (189 ml) and CuO (21.2 g, 0.266 mol) and was transferred to a three-necked flask equipped with mechanical stirring, a nitrogen bleed tube with adjustable flow control and a Claisen adapter. The Claisen adapter was fitted with a distillation apparatus and thermometer to measure the pot temperature. The mixture was heated to 175 °C (pot temperature), the reaction mixture began to effervesce and the nitrogen flow was increased to sweep the reaction vessel. The volatiles (b.p. 140–210 °C, distillate temperature) were collected. Redistillation afforded 2-*tert*-butylfuran (26.7 g, 35%) as a clear liquid: b.p. 117–120 °C (lit.[21] b.p. 119–120 °C); IR (neat) 2965, 1590, 1511, 1463, 1363, 1276, 1161, 1004, 920, 795, 726 cm^{-1}; ^1H NMR ($CDCl_3$), δ 7.33 (m, 1H), 6.28 (dd, J = 3.0, 0.9 Hz, 1H), 5.98 (d, J = 3.0 Hz, 1H), 1.27 (s, 9H).

2-Trimethylsilylfuran. A magnetically stirred solution of furan (13.87 g, 203.7 mmol) in dry THF (100 ml) at −78 °C under argon was treated with *tert*-butyllithium (1.60 M in pentane, 208 mmol). The solution was allowed to warm to room temperature (1 h) and stirred for 3 h. The solution was then cooled to −40 °C and chlorotrimethylsilane (29.9 ml, 235 mmol) was added via a syringe. The solution was allowed to warm to room temperature and stirred for 12 h. A white precipitate separated from the clear solution. The suspension was treated with 10% NH_4Cl solution (100 ml) and the layers were separated. The aqueous layer was extracted with Et_2O (4 × 100 ml). The combined organic extracts were concentrated *in vacuo* and the residual clear oil was digested with fresh Et_2O (200 ml), washed with brine (200 ml), dried (K_2CO_3), filtered and concentrated *in vacuo* to give a clear yellow oil. Kugelrohr distillation (70 °C, 80 Torr) gave 17.02 g (60%) of 2-trimethylsilylfuran as a colorless liquid: b.p. 121–122 °C (lit.[22] b.p. 124–125 °C); IR (neat), 3122, 2974, 2910, 1560, 1467, 1260, 1212, 1156, 1013, 853 cm^{-1}.

2-*tert*-Butyldimethylsilylfuran. A magnetically stirred solution of furan (6.81 g, 100 mmol) in dry THF (50 ml) at −78 °C under argon was treated with *tert*-butyllithium (1.60 M in pentane, 65.0 ml, 104 mmol). The solution was allowed to warm to room temperature (1 h) and stirred for 3 h. The solution was then cooled to −78 °C and *tert*-butyldimethylsilyl chloride (18.13 g, 120.3 mmol) was added in portions. The solution was allowed to warm to room temperature over 1 h, stirred for 12 h and treated with saturated aqueous NH_4Cl (100 ml). The layers were separated and the aqueous layer was further extracted with Et_2O (3 × 100 ml). The combined

organic extracts were concentrated *in vacuo* and the resultant oil was digested with Et_2O (150 ml), washed with brine (150 ml), dried (K_2CO_3), filtered and concentrated *in vacuo*. Distillation at reduced pressure gave 9.49 g (52%) of 2-*tert*-butyldimethylsilylfuran as a clear liquid b.p. 68–72 °C (20 Torr); IR (neat), 2938, 2914, 2842, 1544, 1464, 1458, 1250, 1003, 833, 772, 741 cm^{-1}; ^1H NMR ($CDCl_3$), δ 7.68 (d, J = 1.7 Hz, 1H), 6.67 (d, J = 3.0 Hz, 1H), 6.40 (dd, J = 3.0, 1.7 Hz, 1H), 0.95 (s, 9H), 0.21 (s, 6H); ^{13}C NMR ($CDCl_3$), δ 158.6, 146.6, 120.7, 109.2, 26.4, 16.9. Analysis: calculated for $C_{10}H_{18}OSi$, C 65.87, H 9.95; found, C 66.01, H 9.99%.

8-Fluoro-1-methyl-1,4-dihydronaphthalen-1,4-endoxide and 5-fluoro - 1 - methyl - 1,4 - dihydronaphthalen - 1,4 - endoxide. A magnetically stirred solution of *m*-difluorobenzene (1.50 g, 13.1 mmol) in dry Et_2O (20 ml) was treated at −78 °C under argon with *tert*-butyllithium (1.76 M in pentane, 7.60 ml, 13.4 mmol) via a syringe. The rate of addition was controlled so that the temperature was less than −60 °C throughout. The resultant solution was stirred at −78 °C for 1 h and then treated with freshly distilled 2-methylfuran (2.10 g, 25.6 mmol). The solution was allowed to warm slowly to room temperature (4 h), stirred for 15 h and poured over ice (20 g). The mixture was extracted with Et_2O (4 × 30 ml); the combined organic extracts were washed with brine (100 ml), dried (K_2CO_3), filtered and concentrated *in vacuo* to give a redolent pale yellow oil. The crude oil was subjected to flash chromatography with Et_2O–hexane (1:15, v/v) elution and dried at 60 °C (90 Torr) for 1 h to give 1.54 g (61%) of endoxides, isolated as a mixture of regioisomers (63:37, via integration of the bridgehead protons or methyl protons). The regioisomers were separated by flash chromatography with Et_2O–hexane (gradient elution from 1:20 to 1:15, v/v). Sublimation (50–70 °C, 1.0 Torr) of the major regioisomer (8-fluoro-1-methyl-1,4-dihydronaphthalen-1,4-endoxide) gave the analytical sample as white crystals: IR (KBr), 1631, 1600, 1471, 1217, 943, 848, 797, 779, 729, 675 cm^{-1}; ^1H NMR ($CDCl_3$), δ 7.04–6.88 (m, 3H), 6.84 (d, J = 5.4 Hz, 1H), 6.66 (t, J = 8.4 Hz, 1H), 5.63 (t, J = 1.7 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR ($CDCl_3$), δ 156.3 (d, J = 246.5 Hz, quat.), 154.7 (d, J = 4.3 Hz, quat.), 145.5, 144.3, 135.1 (d, J = 18.6 Hz, quat.), 127.5 (d, J = 6.0 Hz), 116.0 (d, J = 3.1 Hz), 114.2 (d, J = 22.6 Hz), 89.4 (d, J = 2.4 Hz, quat.), 82.0, 16.6. Analysis: calculated for $C_{11}H_9OF$, C 74.99, H 5.15; found, C 74.93, H 5.16%.

Kugelrohr distillation (90–110 °C, 1.0 Torr) of the minor isomer (5-fluoro-1-methyl-1,4-dihydronaphthalen-1,4-endoxide) gave the analytical sample as a clear oil: ^1H NMR ($CDCl_3$), δ 7.02 (dd, J = 5.1, 1.7 Hz, 1H), 6.97–6.93 (m, 2H), 6.77 (d, J = 5.5 Hz, 1H), 6.69–6.62 (m, 1H), 5.87 (d, J = 1.8 Hz, 1H), 1.91 (s, 3H); ^{13}C NMR ($CDCl_3$), δ 155.4 (d, J = 246.6 Hz, quat.), 155.1 (d, J = 4.6 Hz, quat.), 145.6, 143.7, 134.9 (d, J = 20.9 Hz, quat.), 127.4 (d, J = 5.9 Hz), 114.8 (d, J = 2.4 Hz), 113.5 (d, J = 22.8 Hz), 89.7 (bs, quat.), 78.7 (d, J = 4.8 Hz), 15.1. Analysis: calculated for $C_{11}H_9FO$, C 74.99, H 5.15; found, C 74.89, H 5.29%.

8-Fluoro-1-methyl-1,2,3,4-tetrahydronaphthalen-1,4-endoxide. A solution of 8-fluoro-1-methyl-1,4-dihydronaphthalen-1,4-endoxide (65.3 mg, 0.371 mmol) in dry MeOH (5 ml) was treated with crystalline platinum(IV) oxide (35.4 mg) and shaken under hydrogen (3.5 atm) for 12 h. The solution was filtered free of catalyst, the residue was rinsed with MeOH (3 × 10 ml) and the combined organic filtrate was concentrated *in vacuo* to give 47.0 mg (71%) of 8-fluoro-1-methyl-1,2,3,4-tetrahydronaphthalen-1,4-endoxide as a clear oil: ^1H NMR ($CDCl_3$), δ 7.15–7.07 (m, 1H), 6.98 (d, J = 7.1 Hz, 1H), 6.83 (t, J = 8.7 Hz, 1H), 5.32 (dd, J = 5.2, 1.8 Hz, 1H), 2.27–2.16 (m, 1H), 1.96 (s, 3H), 1.80 (dt, J = 4.0, 7.3 Hz, 1H), 1.64–1.53 (m, 1H), 1.47–1.38 (m, 1H); ^{13}C NMR ($CDCl_3$), δ 155.4 (d, J = 246.9 Hz, quat.), 150.3 (d, J = 5.1 Hz, quat.), 132.2 (d, J = 17.7 Hz, quat.), 128.7 (d, J = 6.1 Hz), 114.5 (d, J = 3.0 Hz), 114.3 (d, J = 22.0 Hz), 85.5 (d, J = 2.5 Hz, quat.), 78.5 (d, J = 2.4 Hz), 32.7, 29.2, 18.6; IR (KBr), 1589, 1470, 1389, 1285, 1229, 929, 843, 793, 766 cm^{-1}. Analysis: calculated for $C_{11}H_{11}FO$, C 74.14, H 6.22; found, C 74.02, H 6.31%.

5-Fluoro-1-methyl-1,2,3,4-tetrahydronaphthalen - 1,4 - endoxide. A solution of 5-fluoro-1-methyl-1,4-dihydronaphthalen-1,4-endoxide (77.2 mg, 0.438 mmol) in dry MeOH (5 ml) was treated with crystalline platinum(IV) oxide (34.2 mg) and shaken under hydrogen (3.5 atm) for 12 h. The solution was filtered free of the catalyst and the residue rinsed with fresh MeOH (3 × 10 ml), and the combined organic filtrate concentrated *in vacuo* to give 47.0 mg of a clear oil (60%) identical by ^1H NMR with a sample previously prepared in this laboratory:[23] ^1H NMR ($CDCl_3$), δ 7.19–7.11 (m, 1H), 6.93 (d, J = 7.1 Hz, 1H), 6.84 (t, J = 8.4 Hz, 1H), 5.55 (d, J = 5.0 Hz, 1H), 2.28–2.17 (m, 1H), 1.90–1.75 (m, 1H), 1.84 (s, 3H), 1.56–1.39 (m, 2H).

1-Fluoro-8-methylnaphthalene (4). A magnetically stirred solution of 8-fluoro-1-methyl-1,2,3,4-tetrahydronaphthalen-1,4-endoxide (98.5 mg, 0.553 mmol) in dry MeOH (5 ml) was saturated with hydrogen chloride gas and heated at reflux for 10 h. The solution was then cooled to room temperature, poured into brine (10 ml), treated with Et_2O (10 ml), the layers were separated, and the aqueous layer was further extracted with fresh Et_2O (4 × 20 ml). The combined organic extracts were washed with 10% $NaHCO_3$ (100 ml), brine (100 ml), dried (K_2CO_3), filtered and concentrated *in vacuo* to give a clear oil. The oil was subjected to radial chromatography (hexane elution) and concentrated *in vacuo* to give 62.5 mg (71%) of **4** as a clear oil that was identical by ^1H NMR with that reported by Adcock and Rizvi:[24a] IR (neat), 3064, 1607, 1468, 1381, 1267, 1231, 1018, 817, 767, 755 cm^{-1}; ^1H NMR ($CDCl_3$), δ 7.64 (d, J = 8.1 Hz, 1H), 7.57 (d, J = 8.1 Hz, 1H), 7.36–7.28 (m, 2H), 7.23 (d, J = 6.9 Hz, 1H), 7.09 (ddd, J = 13.5, 7.6, 0.9 Hz, 1H), 2.83 (d, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$), δ 160.5 (d, J = 253.4 Hz, quat.), 136.2 (d, J = 5.0 Hz, quat.), 133.2 (d, J = 3.8 Hz, quat.), 128.5, 126.4, 126.0 (d, J = 3.4 Hz), 125.3 (d, J = 9.1 Hz), 124.5 (d, J = 4.1 Hz), 123.1 (d, J = 12.5 Hz, quat.), 110.8 (d, J = 23.2 Hz), 23.2 (d, J = 12.1 Hz); ^{19}F NMR ($CDCl_3$, 1% Freon 11), δ −112.80.

1-Ethyl-8-fluoro-1,4-dihydronaphthalen-1,4-endoxide and 1-ethyl - 5 - fluoro - 1,4 - dihydronaphthalen - 1,4 - endoxide. A magnetically stirred solution of *m*-difluorobenzene

(1.51 g, 13.2 mmol) in dry Et_2O (20 ml) was treated at −78 °C under argon with *tert*-butyllithium (1.76 M in pentane, 7.50 ml, 13.2 mmol) via a syringe. The rate of addition was controlled so that the temperature was less than −60 °C throughout. The resultant solution was stirred at −78 °C for 15 min and then treated with freshly distilled 2-ethylfuran (2.51 g, 29.1 mmol). The solution was allowed to warm slowly to room temperature (4 h), stirred at room temperature for 16 h and poured over ice (20 g). The mixture was extracted with Et_2O (4 × 30 ml); the combined organic extracts were washed with brine (100 ml), dried (K_2CO_3), filtered and concentrated *in vacuo* to give a redolent yellow oil. The crude oil was subjected to flash chromatography with Et_2O–hexane (1 : 15 v/v) elution and the endoxides were dried (60 °C, 90 Torr, 0.5 h) to give 1.40 g (56%) of 1-ethyl-8-fluoro-1,4-dihydronaphthalen-1,4-endoxide and 0.39 g (15%) of 1-ethyl-5-fluoro-1,4-dihydronaphthalen-1,4-endoxide. Sublimation (55–75 °C, 1.0 Torr) of 1-ethyl-8-fluoro-1,4-dihydronaphthalen-1,4-endoxide gave the analytical sample as a white crystalline solid: ^{1}H NMR ($CDCl_3$), δ 7.03 (dd, J = 5.4, 1.8 Hz, 1H), 7.02–6.98 (m, 1H), 6.97–6.89 (m, 1H), 6.84 (d, J = 5.4 Hz, 1H), 6.66 (t, J = 8.5 Hz, 1H), 5.66 (t, J = 1.8 Hz, 1H), 2.56–2.37 (AB q of q, 2H), 1.16 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$), δ 156.0 (d, J = 245.6 Hz, quat.), 155.0 (d, J = 4.6 Hz, quat.), 144.5, 144.4, 134.1 (d, J = 18.8 Hz, quat.), 127.5 (d, J = 6.5 Hz), 116.0 (d, J = 2.4 Hz), 114.1 (d, J = 23.1 Hz), 93.9 (d, J = 3.1 Hz, quat.), 81.9, 23.3, 9.1; IR (KBr), 1633, 1602, 1473, 1214, 947, 912, 892, 797, 733, 683 cm^{-1}. Analysis: calculated for $C_{12}H_{11}FO$, C 75.77, H 5.83; found, C 75.73, H 5.80%.

Kugelrohr distillation (95–115 °C, 1.0 Torr) of 1-ethyl-5-fluoro-1,4-dihydronaphthalen-1,4-endoxide gave the analytical sample as a clear oil: ^{1}H NMR ($CDCl_3$), δ 7.04 (dd, J = 5.3, 1.4 Hz, 1H), 7.00–6.92 (m, 2H), 6.80 (d, J = 5.6 Hz, 1H), 6.71–6.61 (m, 1H), 5.90 (d, J = 1.5 Hz, 1H), 2.45–2.21 (AB q of q, 2H), 1.16 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$), δ 155.5 (d, J = 246.5 Hz, quat.), 154.2 (d, J = 4.3 Hz, quat.), 144.5, 143.9, 135.4 (d, J = 20.5 Hz, quat.), 127.3 (d, J = 6.3 Hz), 115.3 (d, J = 3.0 Hz), 113.5 (d, J = 22.6 Hz), 93.7 (quat.), 78.6, 22.1, 8.8; IR (KBr), 1631, 1599, 1468, 1280, 1235, 905, 869, 780, 737, 681 cm^{-1}. Analysis: calculated for $C_{12}H_{11}FO$, C 75.77, H 5.83; found, C 75.61, H 5.78%.

1-Ethyl-8-fluoro-1,2,3,4-tetrahydronaphthalen-1,4-endoxide. A solution of 1-ethyl-8-fluoro-1,4-dihydronaphthalen-1,4-endoxide (188.1 mg, 0.989 mmol) in dry MeOH (10 ml) was treated with crystalline platinum(IV) oxide (57.0 mg) and shaken under hydrogen (3.5 atm) for 12 h. The solution was filtered free of catalyst, the residue was rinsed with MeOH (3 × 10 ml) and the combined organic filtrate was concentrated *in vacuo* to give 165.0 mg (87%) of 1-ethyl-8-fluoro-1,2,3,4-tetrahydronaphthalen-1,4-endoxide as a clear oil: ^{1}H NMR ($CDCl_3$), δ 7.16–7.07 (m, 1H), 6.99 (d, J = 7.2 Hz, 1H), 6.83 (t, J = 8.9 Hz, 1H), 5.34 (dd, J = 4.9, 1.6 Hz, 1H), 2.55–2.40 (m, 1H), 2.23–2.09 (m, 2H), 1.88–1.75 (m, 1H), 1.52–1.35 (m, 1H), 1.13 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$), δ 155.1 (d, J = 246.9 Hz, quat.), 150.6 (d, J = 5.5 Hz, quat.), 131.0 (d, J = 18.4 Hz, quat.), 128.7 (d, J = 6.4 Hz), 114.6 (d, J = 2.8 Hz), 114.2 (d, J = 22.1 Hz), 89.7 (d, J = 3.0 Hz, quat.), 78.3 (d, J = 1.9 Hz), 31.0, 28.9, 25.4, 9.2 Analysis: calculated for $C_{12}H_{13}FO$, C 74.98, H 6.82; found, C 75.27, H 6.80%.

8-Ethyl-1-fluoronaphthalene (5). A magnetically stirred solution of 1-ethyl-8-fluoro-1,2,3,4-tetrahydronaphthalen-1,4-endoxide (63.1 mg, 0.328 mmol) in dry MeOH (4 ml) was saturated with hydrogen chloride gas and heated at reflux for 10 h. The solution was then cooled to room temperature, poured into brine (10 ml), treated with Et_2O (20 ml), the layers were separated and the aqueous layer was further extracted with fresh Et_2O (4 × 20 ml). The combined organic extracts were washed with 10% $NaHCO_3$ (80 ml), saturated NaCl (80 ml), dried (K_2CO_3), filtered and concentrated *in vacuo* to give a yellow oil. The oil was subjected to radial chromatography (hexane elution) and concentrated *in vacuo* to give 27.8 mg (49%) of **5** as a clear oil: IR (neat), 2980, 1608, 1591, 1466, 1383, 1268, 1230, 1031, 826, 776 cm^{-1}; ^{1}H NMR ($CDCl_3$), δ 7.68 (d, J = 8.3 Hz, 1H), 7.61 (d, J = 8.2 Hz, 1H), 7.43–7.28 (m, 3H), 7.12 (dd, J = 14.0, 7.6 Hz, 1H), 3.21 (qd, J = 7.5, 3.9 Hz, 2H), 1.34 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$), δ 160.0 (d, J = 253.6 Hz, quat.), 139.5 (d, J = 4.9 Hz, quat.), 136.5 (d, J = 5.3 Hz, quat.), 127.3, 126.5, 126.2 (d, J = 3.0 Hz), 125.2 (d, J = 8.8 Hz), 124.8 (d, J = 4.2 Hz), 122.3 (d, J = 12.8 Hz, quat.), 111.0 (d, J = 23.7 Hz), 29.6 (d, J = 11.4 Hz), 16.4 (d, J = 4.4 Hz); ^{19}F NMR ($CDCl_3$, 1% Freon 11), δ −113.96.

Analysis: calculated for $C_{12}H_{11}F$, C 82.73, H 6.36; found, C 82.61, H 6.41%.

1-*tert*-Butyl-8-fluoro-1,4-dihydronaphthalen-1,4-endoxide and 1-*tert*-butyl-5-fluoro-1,4-dihydronaphthalen-1,4-endoxide. A magnetically stirred solution of *m*-difluorobenzene (1.50 g, 13.1 mmol) in dry THF (40 ml) was treated at −75 °C under argon with *tert*-butyllithium (1.60 M in pentane, 8.80 ml, 14.1 mmol). The rate of addition was controlled so that the temperature was less than −65 °C throughout. The solution was stirred for 2 h and treated with 2-*tert*-butylfuran (3.00 g, 24.1 mmol) via a syringe. The solution was allowed to warm slowly to room temperature (4 h), stirred for 8 h and poured over ice (50 g). The solution was then treated with Et_2O (100 ml), the organic layer was separated and the aqueous layer further extracted with Et_2O (3 × 100 ml). The combined organic extracts were washed with brine (500 ml), dried (K_2CO_3), filtered and concentrated *in vacuo* to give a slightly yellow oil. The crude reaction mixture was subjected to flash chromatography [hexane–CH_2Cl_2 (1 : 1, v/v) elution], which resulted in the isolation of 1.68 g of a mixture of 1-*tert*-butyl-8-fluoro-1,4-dihydronaphthalen-1,4-endoxide and 1-*tert*-butyl-5-fluoro-1,4-dihydronaphthalen-1,4-endoxide in the ratio 8.9 : 1, as determined by integration of the bridgehead region of the ^{1}H NMR spectrum. Radial chromatography (10 : 1 hexane–Et_2O) effected separation of the isomers. Kugelrohr distillation (103–105 °C, 0.8 Torr) of 1-*tert*-butyl-8-fluoro-1,4-dihydronaphthalen-1,4-endoxide gave the analytical sample as a clear oil: IR (neat), 1599, 1462, 1366, 1230, 969, 795, 780, 732, 683 cm^{-1}; ^{1}H NMR ($CDCl_3$), δ 6.97–6.87 (m, 4H), 6.64 (t, J = 8.7 Hz, 1H), 5.61 (t, J = 2.2 Hz, 1H), 1.24 (s, 9H); MS, m/z 218 (M^+), 177, 133, 57 [$(CH_3)_3C^+$]; HR-MS (CI), m/z 219.1197 (calculated for $C_{14}H_{15}FO$, 219.1185).

Kugelrohr distillation (103–105 °C, 0.8 Torr) of 1-*tert*-butyl-5-fluoro-1,4-dihydronaphthalen-1,4-endoxide gave the analytical sample as a clear oil: ^{1}H NMR ($CDCl_3$), δ 7.28–6.94 (m, 4H), 6.70 (t, J = 7.5 Hz, 1H), 5.93 (d, J = 2.1 Hz, 1H), 1.26 (s, 9H); MS, m/z 218 (M^+), 177, 133, 57 [$(CH_3)_3C^+$]; HR-MS (CI), m/z 219.1160 (calculated for $C_{14}H_{15}FO$, 219.1185).

1-*tert*-Butyl-8-fluoro-1,2,3,4-tetrahydronaphthalen-1,4-endoxide. A solution of 1-*tert*-butyl-8-fluoro-1,4-dihydronaphthalen-1,4-endoxide (1.113 g, 5.10 mmol) in anhydrous ethanol (30 ml) was treated with crystalline platinum(IV) oxide (40.0 mg). The suspension was shaken under hydrogen (3.3 atm) for 36 h, the solution was filtered free of the catalyst, the residue was rinsed with fresh MeOH (3 × 10 ml) and the combined organic filtrate was concentrated *in vacuo* to give a clear liquid. Distillation afforded 1.003 g (89%) of 1-*tert*-butyl-8-fluoro-1,2,3,4-tetrahydronaphthalen-1,4-endoxide as a clear liquid: b.p. 114–116 °C (0.20 Torr); IR (neat), 2965, 1592, 1465, 1371, 1243, 1175, 964, 886, 798, 767 cm^{-1}; ^{1}H NMR ($CDCl_3$), δ 7.26–6.98 (m, 2H), 6.86 (dd J = 9.5, 9.0 Hz, 1H), 5.32 (dd, J = 4.9, 1.9 Hz, 1H), 2.15–1.94 (m, 2H), 1.44–1.29 (m, 2H), 1.22 (s, 9H); ^{13}C NMR ($CDCl_3$), δ 154.2 (d, J = 245.0 Hz, quat.), 130.9 (d, J = 2.9 Hz, quat.), 128.7 (d, J = 7.0 Hz, quat.), 114.7 (d, J = 25.7 Hz), 114.7 (d, J = 3.0 Hz), 96.8 (quat.), 77.9, 32.7 (quat.), 29.1, 27.0, 26.1 (d, J = 5.2 Hz). Analysis calculated for $C_{14}H_{17}FO$, C 76.33, H 7.78; found, C 76.38, H 7.97%.

1-*tert*-Butyl-8-fluoronaphthalene (9). A magnetically stirred solution of 1-*tert*-butyl-8-fluoro-1,2,3,4-tetrahydronaphthalen-1,4-endoxide (0.3450 g, 1.57 mmol) in absolute ethanol (5 ml) was saturated with dry hydrogen chloride gas for 0.5 h. The solution was then heated at reflux for 40 h, cooled to room temperature, and poured into water (25 ml). The solution was neutralized with 10% aqueous NaOH and treated with Et_2O (100 ml). The layers were separated and the aqueous layer further extracted with fresh Et_2O (4 × 100 ml). The combined organic extracts were washed with brine (250 ml), dried (K_2CO_3), filtered and concentrated *in vacuo* to give a yellow liquid. The liquid was distilled at reduced pressure and gave 0.2652 g (84%) of **9** as a clear liquid: b.p. 106–108 °C (0.65 Torr); IR (neat), 2960, 1626, 1578, 1375, 1332, 1235, 955, 819, 757 cm^{-1}; ^{1}H NMR ($CDCl_3$), δ 7.80 (ddd, J = 8.3, 2.0, 1.0 Hz, 1H), 7.75 (dd, J = 7.5, 1.0 Hz, 1H), 7.74 (dd, J = 6.9, 1.0 Hz, 1H), 7.52–7.40 (m, 2H), 7.29 (ddd, J = 15.6, 7.6, 1.3 Hz, 1H), 1.56 (d, J = 2.1 Hz, 9H); ^{19}F NMR ($CDCl_3$, 1% Freon 11), δ −96.39. Analysis: calculated for $C_{14}H_{15}F$, C 83.13, H 7.48; found, C 83.19, H 7.53%.

1-Trimethylsilyl-8-fluoro-1,4-dihydronaphthalen-1,4-endoxide and 1-trimethylsilyl-5-fluoro-1,4-dihydronaphthalen-1,4-endoxide. A magnetically stirred solution of *m*-difluorobenzene (0.9983 g, 8.75 mmol) in dry THF (27 ml) was treated at −75 °C under argon with *tert*-butyllithium (1.60 M in pentane, 9.39 mmol) via a syringe. The resultant deep orange solution was stirred at −70 °C for 15 min and then treated with 2-trimethylsilylfuran (2.44 g, 17.4 mmol) via a syringe. The solution was allowed to warm slowly to room temperature (2 h) and stirred at room temperature for 11 h. The solution was then poured over ice (50 g) and treated with brine (50 ml). The layers were separated and the aqueous layer extracted with Et_2O (4 × 75 ml). The ethereal layers were combined, washed with brine (2 × 300 ml), dried (K_2CO_3), filtered and concentrated *in vacuo*. The crude ^{1}H NMR spectrum indicated that 1-trimethylsilyl-8-fluoro-1,4-dihydronaphthalen-1,4-endoxide and 1-trimethylsilyl-5-fluoro-1,4-dihydronaphthalen-1,4-endoxide were present in the relative ratio 5.5:1, as determined by comparison of the integrated bridgehead resonances. Flash chromatography [CH_2Cl_2–hexane (1:1, v/v) elution] followed by radial chromatography (15:1 hexane–Et_2O elution) gave 0.74 g (36%) of pure 1-trimethylsilyl-8-fluoro-1,4-dihydronaphthalen-1,4-endoxide as a clear viscous oil. Kugelrohr distillation (145 °C, 0.25 Torr) gave analytically pure 1-trimethylsilyl-8-fluoro-1,4-dihydronaphthalen-1,4-endoxide: IR (neat), 1629, 1601, 1469, 1254, 1235, 1214, 1150, 953, 920, 849 cm^{-1}; ^{1}H NMR ($CDCl_3$), δ 7.14–6.88 (m, 4H), 6.68 (t, J = 8.7 Hz, 1H), 5.74 (dd, J = 2.4, 1.4 Hz, 1H), 0.41 (s, 9H); ^{13}C NMR ($CDCl_3$, δ 155.7 (d, J = 245.2 Hz, quat.), 154.5 (d, J = 5.0 Hz, quat.), 145.4, 143.0, 136.3 (d, J = 20.6 Hz, quat.), 127.1 (d, J = 6.6 Hz), 116.2 (d, J = 2.4 Hz), 113.7 (d, J = 23.9 Hz), 85.7 (d, J = 3.5 Hz), 83.6, −3.56 (d, J = 3.3 Hz). Analysis: calculated for $C_{13}H_{15}FOSi$, C 66.63, H 6.45; found, C 66.90, H 6.41%.

8-Fluoro-1-trimethylsilyl-1,2,3,4-tetrahydronaphthalen-1,4-endoxide. A solution of 1-trimethylsilyl-8-fluoro-1,4-dihydronaphthalen-1,4-endoxide (94.3 mg, 0.398 mmol) in dry MeOH (2 ml) was treated with platinum(IV) oxide (27.3 mg) and shaken under hydrogen (3.4 atm) for 6 h. The solution was filtered free of the catalyst, the residue was rinsed with fresh MeOH (3 × 10 ml) and the combined organic filtrate was concentrated *in vacuo* to give a clear liquid. The crude reaction product was passed through a pad of silica gel (Et_2O elution) and the filtrate concentrated *in vacuo* to give 85.6 mg (91%) of 8-fluoro-1-trimethylsilyl-1,2,3,4-tetrahydronaphthalen-1,4-endoxide as a clear oil: IR (neat), 2963, 1632, 1592, 1473, 1257, 1242, 964, 857, 804, 774 cm^{-1}; ^{1}H NMR ($CDCl_3$), δ 7.11–6.95 (m, 2H), 6.81 (t, J = 8.6 Hz, 1H), 5.42 (dd, J = 4.6, 2.8 Hz, 1H), 2.04–1.88 (m, 2H), 1.42–1.32 (m, 2H), 0.25 (d, J = 1.4 Hz, 9H); ^{13}C NMR ($CDCl_3$), δ 154.9 (d, J = 246.0 Hz, quat.), 150.9 (d, J = 5.3 Hz, quat.), 133.4 (d, J = 20.5 Hz, quat.), 128.2 (d, J = 6.3 Hz), 114.4 (d, J = 2.8 Hz), 114.0 (d, J = 22.4 Hz), 81.1 (quat.), 80.4, 28.8, 27.4, −3.8 (d, J = 2.5 Hz). Analysis: calculated for $C_{13}H_{17}FOSi$, C 66.06, H 7.25; found, C 65.96, H, 7.26%.

1-Fluoro-8-trimethylsilylnaphthalene (7). A magnetically stirred solution of 8-fluoro-1-trimethylsilyl-1,2,3,4-tetrahydronaphthalen-1,4-endoxide (67.9 mg, 0.287 mmol) in $CHCl_3$ (12 ml) was treated with $AlCl_3$ (12.5 mg, 0.0937 mmol) under argon. The suspension was heated at reflux for 15 min and additional $AlCl_3$ (16.1 mg, 0.121 mmol) was added. The solution was heated at reflux for 5 h, treated with additional $AlCl_3$ (15.6 mg, 0.117 mmol), heated at reflux an additional 3 h, poured into cold water (20 ml) and extracted with CH_2Cl_2

(3 × 20 ml). The combined organic extracts were treated with brine (2 × 50 ml), saturated aqueous $NaHCO_3$ (50 ml) and brine (50 ml), and then were dried (K_2CO_3), filtered and concentrated *in vacuo* to give 49.5 mg (79%) of **7** as a clear oil: ^1H NMR ($CDCl_3$), δ 7.83 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 6.8 Hz, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.45 (dd, J = 8.0, 7.1 Hz, 1H), 7.38 (m, 1H), 7.16 (m, 1H), 0.41 (d, J = 3.8 Hz, 9H); ^{13}C NMR ($CDCl_3$), δ 159.8 (d, J = 249.8 Hz), 135.4 (d, J = 5.7 Hz), 134.6, 134.1, 129.3 (d, J = 3.0 Hz), 125.9, 125.3 (d, J = 9.2 Hz), 124.9 (d, J = 4.3 Hz), 110.5 (d, J = 22.9 Hz), 0.6 (d, J = 10.2 Hz); ^{19}F NMR ($CDCl_3$, 1% Freon 11), δ −109.00; MS, m/z 218 (M^+), 203 ($M^+ - CH_3$), 141 [$M^+ - Si(CH_3)_3$]; HR-MS (CI), m/z 219.1035 (calculated for $C_{13}H_{15}FSi$, 219.1005).

8-Acetyl-1-fluoronaphthalene (6). A magnetically stirred solution of acetyl chloride (0.255 g, 3.25 mmol) in methylene chloride (30 ml) was treated at 0 °C under argon with $AlCl_3$ (1.28 g, 9.60 mmol). The suspension was then treated with the naphthalene **7** (0.569 g, 2.61 mmol) over 2 min. The resultant yellow solution was stirred at 0 °C for 5 h, poured over ice (50 g) and treated with brine (50 ml). The layers were separated and the organic portion was extracted with fresh CH_2Cl_2 (4 × 50 ml). The combined organic extracts were washed with brine (2 × 100 ml), saturated aqueous $NaHCO_3$ (100 ml) and again with brine (100 ml), and then were dried (K_2CO_3), filtered and concentrated *in vacuo* to provide 0.417 g (85%) of **6** as a clear liquid. The compound was spectroscopically identical with that prepared by Adcock *et al.*:[24b] ^1H NMR ($CDCl_3$), δ 7.91 (dt, J = 8.4, 1.5 Hz, 1H), 7.69 (d, J = 8.3 Hz, 1H), 7.52 (dd, J = 8.1, 7.1 Hz, 1H), 7.47 (ddd, J = 8.2, 7.8, 5.2 Hz, 1H), 7.39 (dd, J = 7.1, 1.0 Hz, 1H), 2.63 (d, J = 3.5, 3H); ^{19}F NMR ($CDCl_3$), δ −110.51; ^{13}C NMR ($CDCl_3$), δ 204.9, 157.8 (d, J = 251.6 Hz), 137.4 (d, J = 1.9 Hz), 135.2 (d, J = 4.6 Hz), 129.4 (d, J = 3.0 Hz), 126.5 (d, J = 8.4 Hz), 126.0, 124.4 (d, J = 3.7 Hz), 123.9, 119.2 (d, J = 15.2 Hz), 11.4 (br d, J = 21.4 Hz), 31.4 (m).

1-*tert*-Butyldimethylsilyl-8-fluoro-1,4-dihydronaphthalen-1,4-endoxide and 1-*tert*-butyldimethylsilyl-5-fluoro-1,4-dihydronaphthalen-1,4-endoxide. A magnetically stirred solution of *m*-difluorobenzene (1.002 g, 8.78 mmol) in dry THF (27 ml) was treated at −70 °C under argon with *tert*-butyllithium (1.60 M in pentane, 5.87 ml, 9.39 mmol) via a syringe. The resultant deep orange solution was stirred at −70 °C for 15 min and then treated with 2-*tert*-butyldimethylsilylfuran (3.25 g, 11.7 mmol) via a syringe. The solution was allowed to warm slowly to room temperature (2 h) and stirred at room temperature for 12 h. The solution was then poured over ice (50 g) and treated with brine (50 ml). The layers were separated and the aqueous layer extracted with Et_2O (4 × 75 ml). The ethereal layers were combined, washed with brine (300 ml), dried (K_2CO_3), filtered and concentrated *in vacuo*. The ^1H NMR spectrum of the crude product indicated that 1-*tert*-butyldimethylsilyl-8-fluoro-1,4-dihydronaphthalen-1,4-endoxide and 1-*tert*-butyldimethylsilyl - 5 - fluoro - 1,4 - dihydronaphthalen - 1,4 - endoxide were present in a 7:1 ratio, as determined by the integration of the bridgehead resonances. Flash chromatography with hexane–Et_2O (15:1, v/v) elution gave 0.94 g (39%) of 1-*tert*-butyldimethylsilyl-8-fluoro-1,4-dihydronaphthalen-1,4-endoxide as a clear viscous oil. Kugelrohr distillation (145 °C, 0.25 Torr) gave the pure endoxide: IR (neat), 2920, 2846, 1622, 1590, 1465, 1253, 1234, 1212, 1003, 952, 843 cm^{-1}; ^1H NMR ($CDCl_3$), δ 7.14–6.86 (m, 4H), 6.61 (t, J = 8.7 Hz, 1H), 5.69 (t, J = 2.1 Hz, 1H), 1.00 (s, 9H), 0.32 (d, J = 1.5 Hz, 3H), 0.26 (d, J = 2.0 Hz, 3H); ^{13}C NMR ($CDCl_3$), δ 155.6 (d, J = 245.9 Hz, quat.), 154.3 (d, J = 4.6 Hz, quat.), 146.9, 141.5, 137.5 (d, J = 20.6 Hz, quat.), 127.1 (d, J = 6.5 Hz), 116.2 (d, J = 2.9 Hz), 113.8 (d, J = 24.3 Hz), 86.2 (d, J = 2.8 Hz, quat.), 83.5, 27.0 (d, J = 9.2 Hz), 17.8, −6.8 (d, J = 5.9 Hz), −7.4 (d, J = 5.5 Hz).

8 - Fluoro - 1 - *tert* - butyldimethylsilyl - 1,2,3,4 - tetrahydro - naphthalen-1,4-endoxide. A solution of 1-*tert*-butyldimethylsilyl - 8 - fluoro - 1,4 - dihydronaphthalen - 1,4 - endoxide (74.7 mg, 0.270 mmol) in dry MeOH (3 ml) was treated with platinum(IV) oxide (5.7 mg) and shaken under hydrogen (3.4 atm) for 6 h. The solution was filtered free of the catalyst, the residue was rinsed with fresh MeOH (3 × 10 ml) and the combined organic filtrate was concentrated *in vacuo* to give a clear liquid. Kugelrohr distillation (140 °C, 0.1 Torr) gave 67.6 mg (90%) of 8-fluoro-1-*tert*-butyldimethylsilyl-1,2,3,4-tetrahydronaphthalen-1,4-endoxide as a clear liquid: IR (neat), 2948, 2850, 1625, 1584, 1468, 1249, 1232, 1002, 950, 837 cm^{-1}; ^1H NMR ($CDCl_3$), δ 7.13–7.04 (m, 1H), 7.02–6.96 (m, 1H), 6.81 (dd, J = 9.0, 2.1 Hz, 1H), 5.44 (dd, J = 4.2, 2.0 Hz, 1H), 2.14–2.02 (m, 1H), 1.99–1.88 (m, 1H) 1.40–1.26 (m, 2H), 1.01 (d, J = 2.5 Hz, 9H), 0.26 (bs, 6H); ^{13}C NMR ($CDCl_3$), δ 154.7 (d, J = 246.9 Hz, quat.), 150.1 (d, J = 6.1 Hz, quat.), 134.4 (d, J = 20.1 Hz, quat.), 128.0 (d, J = 6.1 Hz), 114.3 (d, J = 1.7 Hz), 114.1 (d, J = 18.7 Hz), 81.0 (d, J = 3.4 Hz, quat.), 80.1, 30.0, 27.7, 27.3, 18.2, −6.7 (d, J = 6.8 Hz), −7.1 (d, J = 3.5 Hz).

1-Fluoro-8-*tert*-butyldimethylsilylnaphthalene (8). A magnetically stirred solution of 8-fluoro-1-*tert*-butyldimethylsilyl-1,2,3,4-tetrahydronaphthalen-1,4-endoxide (47.5 mg, 0.171 mmol) in $CHCl_3$ (8 ml) was treated with $AlCl_3$ (34.9 mg, 0.261 mmol) under argon. The suspension was heated at reflux for 8 h, poured into cold water (20 ml) and extracted with CH_2Cl_2 (4 × 20 ml). The combined organic extracts were treated with brine (100 ml), saturated aqueous $NaHCO_3$ (100 ml) and brine (100 ml), then dried (K_2CO_3), filtered and concentrated *in vacuo* to give 40.8 mg (90%) of **8** as a clear oil that was homogeneous by TLC and ^1H NMR: ^1H NMR ($CDCl_3$), δ 7.88–7.40 (m, 6H), 0.92 (d, J = 1.7 Hz, 9H), 0.44 (d, J = 5.2 Hz, 6H); ^{19}F NMR ($CDCl_3$, 1% Freon 11), δ −106.69; MS, m/z 260 (M^+), 203 [$M^+ - C(CH_3)_3$], 183 [$M^+ - C(CH_3)_3$, HF], 141 [$M^+ - Si(CH_3)_2C(CH_3)_3$, 100%], 115 [$Si(CH_3)_2C(CH_3)_3^+$], 57 [$C(CH_3)_3^+$]; HR-MS (CI), m/z 261.1481 (calculated for $C_{16}H_{21}FSi$, 261.1475).

1-*tert*-Butyl-5-fluoronaphthalene (10). A solution of 1-*tert*-butyl - 5 - fluoro - 1,4 - dihydronaphthalen - 1,4 - endoxide (0.40 g, 1.8 mmol) in EtOH (100 ml) was charged with 10% Pd/C (0.15 g) and shaken under H_2 (2 atm) for 16 h on a Parr apparatus. The solution was filtered and concentrated *in vacuo* to give 0.28 g (71%) of 1-*tert*-

butyl-5-fluoro-1,2,3,4-tetrahydronaphthalen-1,4-endoxide as a colorless oil; HR-MS, *m/z* 220.1251 (calculated for $C_{14}H_{17}FO$, 220.1264).

Into a solution of this endoxide (0.27 g, 1.2 mmol) in EtOH (50 ml) was bubbled HCl for 30 min. The solution was then heated at reflux for 22 h, poured onto cold water (100 ml), neutralized with NaOH, and extracted with Et_2O (3 × 75 ml). The extract was dried (Na_2SO_4) and concentrated *in vacuo* to give 0.23 g of a yellow oil. Distillation afforded 0.10 g (41%) of **10** as a colorless oil: ^{1}H NMR ($CDCl_3$), δ 8.3–7.9 (m, 2H), 7.6–6.9 (m, 4H), 1.60 (s, 9H); ^{13}C NMR ($CDCl_3$), δ 159.4 (d, J = 249.5 Hz), 146.0 (d, J = 2.4 Hz), 133.0 (d, J = 3.6 Hz), 128.1, 125.5 (d, J = 1.4 Hz), 124.1, 123.9 (d, J = 8.6 Hz), 122.7 (d, J = 3.9 Hz), 119.2 (d, J = 8.1 Hz), 108.1 (d, J = 20.1 Hz), 36.1, 31.8. A satisfactory elemental analysis could not be obtained for this compound.

NMR spectra

NMR spectra were recorded for solutions in $CDCl_3$, referenced to internal $CFCl_3$, on a Bruker AM-300 (282.4 MHz) or a Varian XL-300 (282.2 MHz) spectrometer. Fluorine chemical shifts were assigned based on literature precedents, the observation of through-space spin–spin splitting involving the methyl group protons and the proximate fluorine atom, the observation of a five-bond H–F coupling[23] between a proton and fluorine on C-1 and C-5, respectively, and appropriate proton decoupling experiments.

METHOD OF CALCULATION

The proximity effect of a methyl group on the ^{19}F chemical shift of a fluorine atom attached to an aromatic ring is studied through the local contributions of the ^{19}F magnetic shielding tensor only. These local contributions are calculated using Löwdin's technique[26] of inner projections of the polarization propagator. The application of this technique to study different electronic contributions to the magnetic shielding tensor was thoroughly discussed in previous papers.[8] Therefore, it will not be described in detail here; rather, only a brief account of the main features and approximations is given. The three steps mentioned in the Introduction were undertaken as follows. Calculations were carried out for just a few model compounds (see below).

Step (i): the ground-state wavefunctions of molecules of model compounds were calculated at the standard INDO[15] approximation.

Step (ii): molecular fragments were defined through Engelmann and Contreras's localization procedure,[27] which is a modified version of Verwoerd's.[28] This localization procedure was repeatedly applied within the molecular fragment defined by the side-chains of the model compounds in order to define bonds, lone pairs and antibonding orbitals of that fragment, as explained in Ref. 17.

Step (iii): to make it clear how contributions originated only on the C—F group and on its proximate X side-chain (e.g. the methyl group in **4**) are calculated, this step is described in some detail.

The isotropic magnetic shielding constant of nucleus N can be written as

$$\sigma(\mathrm{N}) = \sigma^{\mathrm{d}}(\mathrm{N}) + \sigma^{\mathrm{p}}(\mathrm{N}) = \frac{1}{3}\sum_{\alpha=1}^{3}[\sigma^{\mathrm{d}}(\mathrm{N}, \alpha\alpha) + \sigma^{\mathrm{p}}(\mathrm{N}, \alpha\alpha)] \tag{1}$$

where $\sigma^{\mathrm{d}}(\mathrm{N})$ and $\sigma^{\mathrm{p}}(\mathrm{N})$ are the diamagnetic and paramagnetic parts of the magnetic shielding constant, respectively.

Since the diamagnetic part is a first-order property, its calculation in terms of LMOs defined in step (ii) is straightforward:

$$\sigma^{\mathrm{d}}_{\mathrm{local}}(\mathrm{N}) = \sum_{i} \sigma^{\mathrm{d}}_{i} \tag{2}$$

where the sum in Eqn. (2) runs over all occupied i LMOs belonging to the molecule under study. Each term of Eqn. (2) depends both on only one occupied LMO and on the diamagnetic operator. In order to obtain its 'local contribution' (see above) the sum in Eqn. (2) must be truncated to include only LMOs belonging to the C—F and X moieties.

The paramagnetic part of the magnetic shielding tensor is a second-order property and in this work it is calculated using the polarization propagation (PP) formalism.[29] It is evaluated at the RPA level (random phase approximation),[29] using GIAOs (gauge invariant atomic orbitals) in the atomic basis set.[30] Such calculations are equivalent to those of the CHF (coupled Hartree–Fock) scheme.[31] Within the PP formalism $\sigma^{\mathrm{p}}(\mathrm{N})$ can be written as[9,29]

$$\sigma_{\mathrm{p}}(\mathrm{N}) = \sum^{mi,\,nj} [V^{mi} W^{mi,\,nj} V^{nj,\,\mathrm{N}} + V^{mi,\,\mathrm{N}} W^{mi,\,nj} V^{nj}] \tag{3}$$

where the sum runs over all vacant m,n and occupied i,j LMOs belonging to the molecule under study, and V^{mi} and $V^{nj,\,\mathrm{N}}$ are the matrix elements of the paramagnetic operator. They depend only on those operators and on the mi,nj LMOs. $W^{mi,\,nj}$ are the singlet polarization propagator matrix elements. Each of them depends on all LMOs belonging to the molecule under study.

Local contributions, i.e. those originated only on the C—F and X moieties, are obtained from Eqn. (3) through Löwdin's[26] inner projections technique as explained elsewhere.[8,9,16,17,27,28] Thus, Eqn. (4) is obtained:

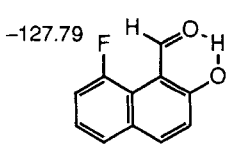
$$\sigma^{\mathrm{p}}_{\mathrm{local}}(\mathrm{N}) = \sum_{mi,\,nj}^{\mathrm{local}} [V^{mi} P^{mi,\,nj} V^{nj,\,\mathrm{N}} + V^{mi,\,\mathrm{N}} P^{mi,\,nj} V^{nj}] \tag{4}$$

where the sum runs only over the LMOs belonging to both the C—F and the X moieties; the matrix elements of the paramagnetic operators, V^{mi} and $V^{nj,\,\mathrm{N}}$, are identical with those of Eqn. (3); $P^{mi,\,nj}$ are the matrix elements of the singlet polarization propagator inner projected onto the subset of occupied and vacant LMOs belonging to both the C—F and X moieties.

Equation (4) can also be written as

$$\sigma^{\mathrm{p}}_{\mathrm{local}}(\mathrm{N}) = \sum_{mi,\,nj}^{\mathrm{local}} \sigma^{\mathrm{p}}_{mi,\,nj}(\mathrm{N}) \tag{5}$$

Table 1. ^{19}F chemical shifts for compounds 1–18, in ppm upfield from CCl_3F



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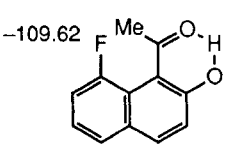

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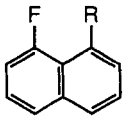
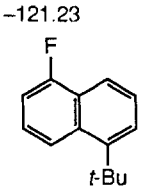


3	R = H	−123.85
4	R = Me	−112.80
5	R = Et	−113.96
6	R = Ac	−110.51
7	R = TMS	−109.00
8	R = TBDMS	−106.69
9	R = *t*-Bu	− 96.39



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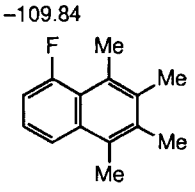

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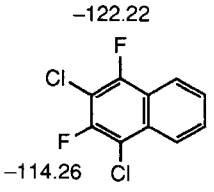

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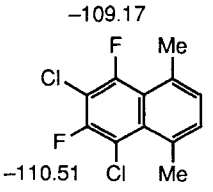

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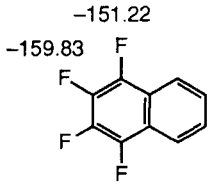

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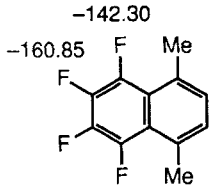

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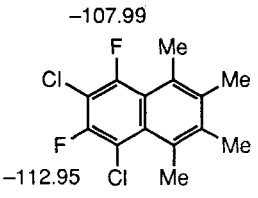

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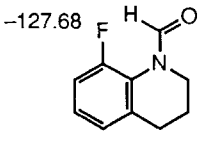

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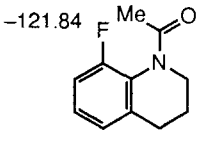


18

Each term of Eqn. (5) depends at most on two occupied i,j and two vacant m,n LMOs (i can be equal to j and m can be equal to n). A comparison between $W^{mi,nj}$ and $P^{mi,nj}$ yields an idea of the influence of the non-local part of the molecule on $\sigma^{p}_{mi,nj}(N)$.

Rearranging terms in Eqn. (4), $\sigma^{p}_{mi,nj}$ can be written as the product of two different factors:

$$\sigma^{p}_{mi,nj}(N) = P_{mi,nj}U_{mi,nj}(N) \qquad (6)$$

where $U_{mi,nj}$ depends both on mi,nj LMOs and on the paramagnetic operators while the matrix elements of the projected polarization propagator, $P^{mi,nj}$, do not depend on the paramagnetic operator, but depend on all molecular orbitals of the molecular fragment on which it is projected.

RESULTS AND DISCUSSION

Fluorine chemical shifts for compounds **1–18** are shown in Table 1. An adequate comparison of these chemical shifts shows that the proximity of a methyl group to a fluorine atom produces a significant deshielding effect.

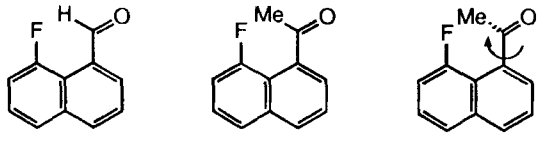
Table 2. Comparison of ^{19}F chemical shifts in pairs of different compounds

Entry	Compounds	Difference in shielding (ppm)
i	18–17	5.84
ii	15–14	8.92
iii	4–3	11.05
iv	11–10	11.39
v	13–12	13.05
vi	16–12	14.23
vii	7–3	14.85
viii	8–3	17.16
ix	2–1	18.17
x	9–3	27.46

They are compared in Table 2 by taking the differences in chemical shifts for pairs of compounds which differ in the degree of crowding but which are otherwise similar. It is observed that the methyl effect strongly depends on the F—Me distance. For instance, the difference (i) between **18** and **17** indicates that the replacement of the formyl proton by a Me group deshields the fluorine nucleus by 5.84 ppm. The same replacement converting

1 to **2**, where the hydroxyl hydrogen bond forces a much closer proximity than in **18**, yields a difference of 18.17 ppm (ix). There is other evidence[18] that **18** is nonplanar, notably the temperature dependence of ^1H and ^{13}C NMR spectra and the low value of $^6J(F, CH_3)$. It is also interesting to compare the deshielding effects produced by the *tert*-butyldimethylsilyl and *tert*-butyl groups, differences (viii) and (x), respectively. The latter produces a deshielding effect larger by about 10 ppm than the former. This difference can be rationalized by recalling that the Si—C_{aryl} bond length is about 0.3Å longer (1.84 Å vs 1.52 Å), than the corresponding bond in the *tert*-butyl compound,[25] so the silicon methyl groups are not held as close to the fluorine.

In order to obtain an insight into factors defining the methyl proximity effect, we calculated the local contributions of the ^{19}F magnetic shielding constants in compounds **1a**, **2a**, **2a'**, **3** and **4** (**1a** is the same as **1** but without the OH group, and **2a** and **2a'** are the same as **2** without the OH group).



1a **2a** **2a'**

The local diamagnetic and local paramagnetic contributions to the ^{19}F magnetic shielding constants for **1a**, **2a**, **2a'**, **3** and **4** are shown in Table 3. They were calculated as explained above. Structural data were taken as follows. In all cases the ring geometry was taken from the experimental data for naphthalene.[32] In **1a**, **2a**, **3** and **4**, side-chain geometries were built up from the standard model of Pople and Gordon.[33] Since in **2a** the standard model yields too close a proximity between the fluorine nucleus and the methyl group, slight changes in the FCC and $C_{carbonyl}CC_{aromatic}$ angles were introduced. In **2a'** these changes were 5° and 3°, respectively, occurring in such a way that the Me group and the F atom are not so compressed as in **2a**. An increase in bond angles to relieve *peri* interactions has been reported in several compounds.[34]

In all five cases, compounds **1a**, **2a**, **2a'**, **3** and **4**, local contributions were calculated using all LMOs belonging to the side-chains. For instance, in **1a** local components were calculated using all LMOs belonging to the C—F and CHO moieties, including in the latter the C—C bond and antibond. The difference observed between the local contribution to the magnetic shielding constant in **2a** and **2a'** shows a strong dependence of the methyl deshielding effect on the Me—F distance. It is worth noting that the close agreement between calculated and experimental methyl proximity effects, displayed in Table 3, supports our assumption (see Introduction) that this effect, being a proximity one, does not require a large basis set to be properly described. It is also important to note that the local contribution to the diamagnetic part of the magnetic shielding constant is almost unaffected by the proximity to a methyl group. This effect is mainly defined by the increase in the absolute values of the paramagnetic term, which, being negative, is a deshielding effect. Further insight into the origin of this deshielding effect can be obtained by comparing the different terms of Eqn. (5). In each case three different types of terms can be considered: (a) fluorine contributions, $\sigma^{L(F)}_{mi,nj}$, where all *mi*, *nj* LMOs belong to the CF moiety; (b) the proximate X group contribution, $\sigma^{L(X)}_{mi,nj}$, where all *mi*, *nj* LMOs belong to the X group (e.g. the CHO moiety in **1a**); in all cases studied here, such $\sigma^{L(X)}_{mi,nj}$ contributions are negligible; and (c) cross-contributions, $\sigma^{L(FX)}_{mi,nj}$, where *mi*, *nj* LMOs belong either to the CF group or to the X group.

In Table 4 the two main $\sigma^{L(F)}_{mi,nj}$ terms, together with the sum of all cross-terms, are shown for **1a**, **2a**, **2a'**, **3** and **4**. When comparing these three types of contributions in **2a** and **2a'**, it is observed that each of them depends strongly on the F—Me distance. However, the sum of all cross-terms is the most sensitive one.

Table 4 also illustrates in parentheses the $P_{mi,nj}$ factors [see Eqn. (6)] corresponding to term I, i.e. for $m = n =$ C—F antibonding LMO, and $i = j =$ LP(π) occupied LMO. It is observed that these $P_{mi,nj}$ factors in **1a**, **2a**, and **2a'** differ at most by a few parts per thousand; also observed is a similar behavior for term II (the corresponding $P_{mi,nj}$ terms are not shown since each of these terms is actually a sum of two contributions originated in the two in-plane lone pairs). Therefore, the methyl proximity effect on the fluorine contributions, $\sigma^{L(F)}_{mi,nj}$, originates mainly on the $U_{mi,nj}$ terms of Eqn. (6). This result is in line with the qualitative conclusions drawn by Li and Chesnut,[4] who ascribed the deshielding effect mainly to an increase in $1/r^3$ owing to the

Table 3. Local diamagnetic and paramagnetic contributions to the ^{19}F magnetic shielding constants in compounds in 1a, 2a, 2a', 3 and 4 (in ppm)

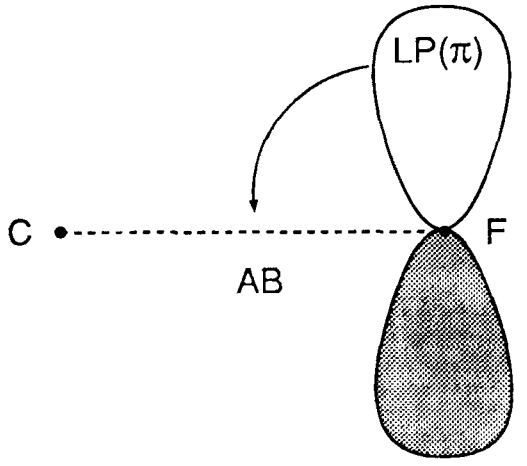
Parameter	1a	2a	2a'	3	4
σ^d_L	474.37	474.81	474.86	474.29	474.57
σ^p_L	−244.87	−272.28	−263.38	−232.88	−244.75
$\sigma_L = \sigma^d_L + \sigma^p_L$	229.50	202.53	211.48	241.41	229.82
Difference	26.97	18.02[a]		11.59	
Exp.	18.17[b]	18.17[b]		11.05[c]	

[a] Differences between σ_L in **1a** and σ_L in **2a'**.
[b] See difference ix in Table 2.
[c] See difference iii in Table 2.

Table 4. Main $\sigma^{L(F)}_{mi,nj}$ contributions and sum of cross contributions $\sigma^{L(F,X)}_{mi,nj}$ to the local paramagnetic term in compounds 1a, 2a, 2a', 3 and 4 (in ppm)[a]

Compound	$\sigma^{L(F)}_{mi,nj}$ (I)[b]	$\sigma^{L(F)}_{mi,nj}$ (II)[c]	σ^{L} (cross)[d]
1a	−125.15 (1.8083)	−119.50	0.55
2a	−131.04 (1.8170)	−127.61	−13.10
2a'	−128.25 (1.8184)	−122.35	−4.53
3	−119.59 (1.7430)	−112.81	−0.46
4	−125.43 (1.8172)	−119.15	−0.15

[a] The corresponding values of the inner projected polarization propagator [see Eqn. (6)] are shown in parentheses.
[b] In I, *mi,nj* are as follows: $m = n$ = C–F antibond; $i = j$ = LP(π).
[c] In II, *mi nj* are as follows: $m = n$ = C—F antibond; $i = j$ = either of both in-plane LPs. Therefore, this term actually corresponds to the sum of the two contributions. It should be noted that both in-plane LPs are not well separated by the localization procedure.
[d] This corresponds to the sum of all cross-terms.



Scheme 1

contraction of orbitals involved in the repulsive interaction. In fact, the $1/r^3$ dependence is contained only in the $U_{mi,nj}$ factor. For term I in **1a**, **2a** and **2a'** a pictorial representation of the influence of $1/r^3$ in the $U_{mi,nj}$ factor of Eqn. (6) can be obtained as follows. Its dependence comes from

$$\langle (C—F)^* \mid L_{N_z}/r^3 \mid LP(\pi) \rangle$$

where the z-axis is perpendicular to the molecular plane, (C—F)* is the C—F antibonding orbital and LP(π) is a π-type fluorine lone pair. This expression corresponds to the average values of $1/r^3$ calculated using the π-type lone pair rotated 90° around the z-axis and the C—F antibonding orbital (see Scheme 1). When this average value is increased (smaller r), keeping almost constant the $P_{mi,nj}$ factor of Eqn. (6), the absolute value of the paramagnetic term is increased, yielding a deshielding effect.

The difference of the $P_{mi,nj}$ factor of term I in **3** is larger than that in all other compounds shown in Table 4. In **3** the X group is just the *peri* C—H bond and its antibonding orbital and the small size of this 'side-chain' enters through the $P_{mi,nj}$ term. On the other hand, cross-terms are significant only when there is a large steric crowding between the Me and the CF groups. Their total contributions increase rapidly when the F—Me distance decreases.

It is interesting to compare the *peri* effect of the acetyl group in **6** with the steric *ortho* effect in *o*-fluoroacetophenone. Recently, the ^{19}F SCS (substituent chemical shift) of several *ortho*-, *meta*- and *para*-monosubstituted fluorobenzenes have been reported by Fifolt *et al.*[35] From these values, *ortho* steric effects can be estimated by considering that *ortho* electronic effects will, in general, be similar to those at the *para* positons (*ortho–para* equivalence). Fifolt *et al.*[35] reported for fluoroacetophenone the following effects: *o*-SCS +3.2 ppm and *p*-SCS +6.7 ppm. Therefore, it can be estimated that the steric *ortho* effect for the acetyl moiety is *ca.* −3.5 ppm (negative means a shielding effect). Comparison of chemical shifts reported in Table 1 for compounding **6** and **3** shows that the *peri* effect of the acetyl moiety corresponds to a deshielding effect of 13.34 ppm (*peri*-SCS +13.34 ppm). It is important to recall that in *o*-fluoroacetophenone the methyl group is placed in an all-*cis* conformation with respect to the F atom.[36–38] A similar conformation can be expected in **6** by comparison with **2** and **18**.[18] This change in sign of the steric substituent effect when going from the *ortho* to the *peri* effect would indicate, according to Li and Chesnut,[2] that whereas in **6** the van der Waals interaction is repulsive, in *o*-fluoroacetophenone that interaction is attractive.

Acknowledgements

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REFERENCES

1. M. J. Foster, in *Nuclear Mag Magnetic Resonance*, edited by G. A. Webb, Specialist Periodical Report, Vol. 18, Chapt. 2. Royal Society of Chemistry, London (1989).
2. S. Li and D. B. Chesnut, *Magn. Reson. Chem.* **23**, 625 (1985).
3. N. L. Allinger, *J. Am. Chem. Soc.* **99**, 8127 (1977).
4. S. Li and D. B. Chesnut, *Magn. Reson. Chem.* **24**, 93 (1986).
5. D. W. Boykin, R. L. Hertzler, J. K. Delphon and E. J. Eisenbraun, *J. Org. Chem.* **54**, 1418 (1989).
6. D. W. Boykin, B. Dewprashad and E. J. Eisenbraun, *J. Org. Chem.* **55**, 425 (1990).
7. A. L. Baumstark, M. Dotrong, R. R. Stark and D. W. Boykin, *Tetrahedron Lett.* 2143 (1988).
8. (a) M. B. Ferraro, M. A. Natiello and R. H. Contreras, *Int. J. Quantum Chem.* **30**, 77 (1986); (b) M. B. Ferraro, D. G. De Kowalewski, R. H. Contreras and F. S. Ortiz, *Chem. Phys.* **118**, 325 (1987).

9. R. H. Contreras, M. C. Ruiz de Azúa, C. G. Giribet, M. B. Ferraro and A. C. Diz, in *Quimica Teorica*, edited by S. Fraga, Vol. II, Chapt. 16. CSIC, Madrid (1989).
10. W. Kutzelnigg, *Isr. J. Chem.* **19**, 193 (1980); M. Schindler and W. Kutzelnigg, *J. Am. Chem. Soc.* **105**, 1360 (1983).
11. T. D. Bouman and A. E. Hansen, *Chem. Phys. Lett.* **149**, 510 (1988).
12. U. Fleischer and M. Schindler, *Chem. Phys.* **120**, 103 (1988).
13. R. H. Contreras, M. A. Natiello and G. E. Scuseria, *Magn. Reson. Rev.* **9**, 239 (1985).
14. M. D. Beer, CNINDO 3.3.3 Program, NMR Program Library, Daresbury, Warrington, UK.
15. J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory*. McGraw-Hill, New York (1970).
16. (a) M. C. Ruiz de Azúa, A. C. Diz, C. G. Giribet, R. H. Contreras and I. D. Rae, *Int. J. Quantum. Chem.* **S20**, 585 (1986); (b) A. C. Diz, M. C. Ruiz de Azúa, C. G. Giribet and R. H. Contreras, *Int. J. Quantum Chem.* **37**, 663 (1990).
17. L. B. Krivdin, S. V. Zinchenko, V. V. Shcherbakov, G. A. Kalabin, R. H. Contreras, M. F. Tufro, M. C. Ruiz de Azúa and C. G. Giribet, *J. Magn. Reson.* **84**, 1 (1989).
18. I. D. Rae, A. Staffa, A. C. Diz, C. G. Giribet, M. C. Ruiz de Azúa and R. H. Contreras, *Aust. J. Chem.* **40**, 1923 (1987).
19. (a) G. W. Gribble, M. P. Sibi, S. Kumar and W. J. Kelly, *Synthesis* 502 (1983); (b) G. W. Gribble, R. W. Allen, C. S. Le Houllier, J. T. Eaton, N. R. Easton, Jr., R. I. Slayton and M. P. Sibi, *J. Org. Chem.* **46**, 1025 (1981); (c) G. W. Gribble, W. J. Kelly and M. P. Sibi, *Synthesis* 143 (1982); (d) G. W. Gribble, D. J. Keavy, S. E. Branz, W. J. Kelly and M. A. Pals, *Tetrahedron Lett.* 6227 (1988).
20. J. E. Fitzpatrick, D. J. Milner and P. White, *Synth. Commun.* **12**, 489 (1982).
21. H. Gilman and N. O. Calloway, *J. Am. Chem. Soc.* **55**, 4197 (1933).
22. R. A. Benkeser and R. B. Currie, *J. Am. Chem. Soc.* **70**, 1780 (1948).
23. G. W. Gribble and W. J. Kelly, *Tetrahedron Lett.* 2475 (1981).
24. (a) W. Adcock and S. Q. A. Rizvi, *Aust. J. Chem.* **26**, 2659 (1973); (b) W. Adcock, D. G. Matthews and S. Q. A. Rizvi, *Aust. J. Chem.* **24**, 1829 (1971).
25. L. E. Sutton, *Tables of Interatomic Distances and Configuration in Molecules and Ions*. Chemical Society, London (1958); Supplement (1965).
26. P. O. Löwdin, *J. Math. Phys.* **3**, 969 (1962).
27. A. R. Engelmann and R. H. Contreras, *Int. J. Quantum Chem.* **23**, 1033 (1983).
28. W. S. Verwoerd, *Chem. Phys.* **44**, 151 (1979).
29. J. Oddershede, *Adv. Quantum Chem.* **11**, 275 (1978).
30. F. London, *J. Phys. Radium* **8**, 397 (1937).
31. H. Nakatsuji, *J. Chem. Phys.* **61**, 3728 (1974).
32. W. J. Cruickshank and R. A. Sparks, *Proc. R. Soc. London, Ser. A* 258 (1960).
33 J. A. Pople and M. Gordon, *J. Am. Chem. Soc.* **89**, 4253 (1967).
34. M. B. Jameson and B. R. Penfold, *J. Chem. Soc.* 528 (1965).
35. M. J. Fifolt, S. A. Sojka, R. A. Wolfe, D. S. Hojnicki, J. F. Bieron and F. J. Dinan, *J. Org. Chem.* **54**, 3019 (1989).
36. T. Schaefer, J. Peeling and T. A. Wildman, *Org. Magn. Reson.* **22**, 477 (1984).
37. D. Mirarchi and G. L. D. Ritchie, *J. Mol. Struct.* **118**, 303 (1984).
38. R. H. Contreras, C. G. Giribet, M. A. Natiello, J. Perez, I. D. Rae and J. A. Weigold, *Aust. J. Chem.* **38**, 1779 (1985).