Long-Range NMR Coupling between a Cyclopropyl Proton and a Proton next to the Ring in a Number of 2,2-Disubstituted 1,1-Dihalocyclopropanes

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Analysis of the proton NMR spectra of 2,2-dibromo-1-propylcyclopropanecarboxylic acid, 2,2-dichloro-1-propylcyclopropanecarboxylic acid and 12 1,1-dihalo-2-phenylcyclopropane derivatives with an additional substituent attached to C-2 revealed a long-range coupling (^4J) between the cyclopropyl proton *cis* to the carboxyl or the phenyl group and one of the protons next to the three-membered ring. The absolute value of this coupling turned out to be sensitive to the properties of the substituents attached to the ring and varied from 0.56 to 1.54 Hz. By using structural data obtained by X-ray crystallography for four of the compounds and the correlations of Bystrov and Stepanyants the variation of ^4J has been related to structural and conformational differences. The conformational changes are mainly due to steric interactions, which in part can be rationalized on the basis of semiempirical calculations (AM1) of the rotation of phenyl substituents in model compounds.

The structures of the four cyclopropanes were determined from single-crystal diffraction data obtained at low temperature. 2-(2,2-Dibromo-1-phenylcyclopropyl)-ethanoic acid: $C_{11}H_{10}Br_2O_2$, orthorhombic, space group *Pbca*, a = 8.082(1), b = 15.591(2), c = 18.264(3) Å, (t = −140 °C), Z = 8. 2-(2,2-Dichloro-1-phenylcyclopropyl)ethanoic acid: $C_{11}H_{10}Cl_2O_2$, orthorhombic, space group *Pbca*, a = 8.219(2), b = 14.956(3), c = 18.431(4) Å, (t = −135 °C), Z = 8. 2-Bromomethyl-1,1-dichloro-2-phenylcyclopropane: $C_{10}H_9BrCl_2$, orthorhombic, space group *Pbca*, a = 9.263(2), b = 11.423(2), c = 20.091(3) Å, (t = −135 °C), Z = 8. 2,2-Dichloro-1-phenylcyclopropylmethyl 4-nitrobenzoate: $C_{17}H_{13}Cl_2NO_4$, monoclinic, space group $P2_1/n$, a = 6.210(1), b = 28.886(9), c = 9.022(3) Å, (t = −135 °C), Z = 4. The structures were refined to R values of 0.051, 0.052, 0.048 and 0.042, respectively.

Long-range coupling between a ring proton and a proton belonging to a substituent attached to the ring is generally not observed in the proton NMR spectra of cyclopropanes. Most of the few cyclopropanes that violate this rule[1–5] have an sp^2-hybridized carbon atom next to the ring; this mediates long-range coupling rather effectively owing to electron delocalization in the π system.[6–8] It was therefore somewhat surprising to observe that the proton NMR spectrum of 1,1-dibromo-2-phenyl-2-(2-propenyl)cyclopropane (**1**),[9] which is lacking such a π system, does exhibit coupling between the cyclopropyl proton *cis* to the phenyl group and the methylene group next to the three-membered ring. Even more surprising, however, was the observation that the ring proton is significantly coupled only to one of the methylene protons. This could indicate that the methylene group assumes almost a fixed conformation in solution, in spite of the fact that inspection of accurate molecular models indicates that such a group next to the cyclopropane ring is able to rotate almost freely by at least some 150°. We therefore became interested in preparing a number of similar compounds to find out if such a long-range spin–spin interaction is present in other 2,2-disubstituted 1,1-dihalocyclopropanes and, on the basis of these results, to try to gain more knowledge about the reason for this unusual coupling. The structures of the compounds studied are shown in Scheme 1.

Experimental

Equipment. IR spectra were recorded on a Shimadzu IR-435 spectrophotometer. ^{1}H NMR spectra were obtained at 298 K on a Bruker WM-500 NMR spectrometer operating at 500.135 MHz. ^{13}C NMR spectra were recorded at the same temperature on a Jeol FX90Q spectrometer operating at 22.50 MHz for all compounds except **7**; its spectrum was recorded on a Bruker WM-500 NMR spectrometer operating at 125.759 MHz. Variable-temperature studies were carried out on a Jeol FX90Q spectrometer operating at 89.55 MHz. $CDCl_3$ was used as solvent unless otherwise stated. Chemical shifts are reported in ppm

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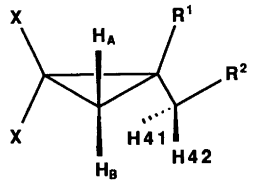

Compound	X	R^1	R^2
1	Br	Ph	$CH=CH_2$
2	Cl	Ph	$CH=CH_2$
3	Br	Ph	CH_2CH_2OH
4	Br	Ph	CH_2COOH
5	Br	Ph	COOH
6	Cl	Ph	COOH
7	Br	Ph	Br
8	Cl	Ph	Br
9	Br	Ph	OH
10	Cl	Ph	OH
11	Br	Ph	CH_2CH_3
12	Cl	Ph	CH_2CH_3
13	Cl	Ph	$OOCC_6H_4NO_2$
14	Br	COOH	CH_2CH_3
15	Cl	COOH	CH_2CH_3

Scheme 1.

operating at 89.55 MHz. $CDCl_3$ was used as solvent unless otherwise stated. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS), which was used as internal reference. GC analyses were performed on a Carlo Erba HRGC 5300 Mega series gas chromatograph equipped with FID and a Chrompack CP-Sil 5CB fused silica coloumn (26 m×0.32 mm i.d.) and connected to an LDC/Milton Roy integrator. Mass spectra were obtained on a VG 7070H Micromass spectrometer and a VG Tribrid mass spectrometer operated in the EI mode at 70 eV. The spectra are reported as *m/z* (% rel. int.).

Synthesis

1,1-Dibromo-2-phenyl-2-(2-propenyl)cyclopropane (**1**) was prepared as described earlier.[9] ^{1}H NMR (89.55 MHz, toluene-d_8, 300 K): δ 1.43 (1 H, d, *J* 7.57 Hz), 1.76 (1 H, dd, *J* 1.22 and 7.57 Hz), 2.22–2.46 (1 H, m), 2.62–2.89 (1 H, m), 4.64–4.87 (2 H, m), 5.28–5.65 (1 H, m),6.90–7.25 (5 H, m).

1,1-Dichloro-2-phenyl-2-(2-propenyl)cyclopropane (**2**) was prepared from 6.56 g (46 mmol) 2-phenyl-1,4-pentadiene[10] using Makosza's method.[11] The product was isolated in 40 % yield by distillation, b.p. 60–61 °C/0.23 mmHg. IR (film): 3090 (s), 3060 (s), 3020 (s), 2960 (m), 2900 (m), 1640 (s), 1600 (m), 1580 (w), 1495 (s), 1443 (s), 1420 (s), 1100 (s), 1038 (s), 998 (s), 987 (s), 917 (s), 775 (s), 748 (s), 715 (s), 698 (s) cm^{-1}; ^{1}H NMR: δ 1.64 (1 H, d, *J* 7.28 Hz), 1.90 (1 H, dd, *J* 1.28 and 7.28 Hz), 2.50 (1 H, ddt, *J* 1.09, 7.85 and 14.34 Hz), 2.87 (1 H, ddq, *J* 1.28, 6.27 and 14.34 Hz), 4.93–4.99 (2 H, m), 5.61–5.69 (1 H, m), 7.25–7.37 (5 H, m): ^{13}C NMR: δ 31.1, 40.4, 42.7, 65.6, 117.6, 127.2, 128.1, 129.5, 133.9, 139.0; MS: 226 (0.4, M^+), 193 (22), 191 (69), 187 (9), 185 (14), 179 (2), 177 (8), 165 (3), 163 (11), 156 (10), 155 (59), 153 (13), 150 (100), 141 (12), 130 (54), 129 (100), 127 (52), 116 (12), 115 (91). Anal. $C_{12}H_{12}Cl_2$: C, H.

3-(2,2-Dibromo-1-phenylcyclopropyl)propane-1-ol (**3**) was prepared from **1** (2.21 g, 7.0 mmol) using borane dimethylsulfide as described in the literature.[12] The product (1.10 g, 47 %), was obtained pure after column chromatography (SiO_2, $CHCl_3$), 2390 (m), m.p. 60–63 °C. IR (KBr): 3400 (s), 3060 (w), 2960 (m), 2870 (m), 1600 (w), 1495 (w), 1445 (s), 1420 (w), 1055 (s), 1023 (m), 955 (w), 770 (m), 700 (s) cm^{-1}; ^{1}H NMR: δ 1.15 (1 H, broad s, OH), 1.43–1.59 (2 H, m), 1.78 (1 H, d, *J* 7.52 Hz), 1.85 (1 H, ddd, *J* 5.8, 10.8 and 13.67 Hz), 2.10 (1 H, dd, *J* 1.50 and 7.52 Hz), 2.21 (1 H, dddd, *J* 1.50, 5.1, 10.37 and 13.67 Hz), 3.57 (2 H, m), 7.25–7.38 (5 H, m); ^{13}C NMR: δ 30.3, 33.1, 36.3, 36.8, 39.6, 62.2, 127.3, 128.3, 129.3, 140.3; MS: 277 (3), 275 (5), 254 (5), 252 (6), 208 (7), 195 (23), 193 (22), 173 (45), 172 (14), 156 (46), 154 (100), 129 (62), 117 (23). Anal. $C_{12}H_{14}Br_2O$: C, H.

3-(2,2-Dibromo-1-phenylcyclopropyl)propanoic acid (**4**) was prepared from **3** (0.67 g, 2.0 mmol) using chromic acid as described in the literature.[13] Oxidation overnight gave 0.23 g recovered starting material and 0.27 g (58 % based on consumed material) of **4**, m.p. 122–126 °C. When the compound was allowed to crystallize after melting, the melting point changed to 126–127 °C. IR (KBr): 3300–2200 (m), 3020 (m), 2970 (m), 2915 (m), 1720 (s), 1697 (s), 1498 (w), 1455 (w), 1445 (m), 1423 (m), 1305 (m), 1278 (w), 1215 (m), 760 (w), 695 (m) cm^{-1}; ^{1}H NMR: δ 1.77 (1 H, d, *J* 7.62 Hz), 2.02 (1 H, dd, *J* 1.42 and 7.62 Hz), 2.07 (1 H, m), 2.22 (2 H, m), 2.39 (1 H, m), 7.3 (5 H, m), 10.62 (1 H, broad s); ^{13}C NMR: δ 31.7, 33.1, 35.2, 35.3, 39.0, 127.7, 128.5, 129.4, 139.3, 178.6; MS: 275 (1), 268 (8), 266 (10), 264 (3), 213 (5), 188 (3), 187 (22), 161 (100), 143 (15), 142 (17), 141 (37), 128 (24), 115 (37). The compound as obtained was not sufficiently pure for elemental analysis.

2-(2,2-Dibromo-1-phenylcyclopropyl)ethanoic acid (**5**) was prepared from **1** (3.80 g, 12 mmol) using potassium permanganate.[14] Benzyltriethylammonium chloride (TEBA) was used as catalyst. After five days, extraction with ether and isolation of acidic material in the usual way gave 1.2 g recovered starting material and 1.33 g (48 % based on consumed material) of **5**, m.p. 159–161 °C. IR (KBr): 3300–2300 (w), 3030 (w), 2970 (w), 2930 (w), 1720 (s), 1500 (w), 1445 (w), 1425 (m), 1338 (w), 1260 (m), 1225 (m), 1030 (w), 1015 (w), 777 (w), 702 (m), 600 (w) cm^{-1}; ^{1}H NMR: δ 2.05 (1 H, d, *J* 8.29 Hz), 2.29 (1 H, dd, *J* 1.40 and 8.29 Hz), 2.92 (1H, d, *J* 16.33 Hz), 3.25 (1 H, dd, *J* 1.40 and 16.33 Hz), 7.4 (5 H, m); ^{1}H NMR (89.55 MHz, toluene-d_8, 300 K): δ 1.59 (1 H, d, *J* 8.30 Hz), 1.92 (1 H, dd, *J* 1.23 and 8.30 Hz), 2.51 (1 H, d, *J* 16.4 Hz), 2.97 (1 H, dd, *J* 1.23 and 16.4 Hz), 7.0 (5 H, m); ^{13}C NMR: δ 33.1 (CH_2), 34.3 (C), 36.2 (C), 44.9 (CH_2), 127.8 (CH), 128.4 (2×CH), 129.5 (2×CH), 139.1 (C), 176.4 (C); MS: 254 (1), 210 (17), 208

(22), 206 (5), 195 (3), 173 (4), 130 (18), 129 (100), 115 (11), 103 (14), 102 (25), 101 (6). Anal. $C_{11}H_{10}Br_2O_2$: C, H.

2-(2,2-Dichloro-1-phenylcyclopropyl)ethanoic acid (**6**) was prepared from **2** (376 mg, 1.7 mmol) using potassium permanganate.[14] Benzyltriethylammonium chloride (TEBA) was used as catalyst. After six days, extraction with ether and isolation of the acidic material in the usual way afforded 113 mg recovered starting material and 198 mg (68 % based on consumed material) of **6**, m.p. 105–107 °C (phase transition at 87–90 °C). IR (KBr): 3300–2400 (w), 3020 (w), 2960 (w), 2930 (w), 1717 (s), 1600 (w), 1580 (w), 1500 (w), 1450 (w), 1425 (w), 1337 (w), 1265 (m), 1227 (m), 1020 (w), 780 (w), 760 (w), 697 (w), 610 (w) cm^{-1}; ^1H NMR: δ 1.88 (1 H, d, *J* 7.94 Hz), 2.11 (1 H, dd, *J* 1.31 and 7.94 Hz), 2.88 (1 H, d, *J* 16.49 Hz), 3.18 (1 H, dd, *J* 1.31 and 16.49 Hz), 7.3 (5 H, m), 10.8 (1 H, broad s); ^{13}C NMR: δ 31.5 (CH_2), 37.0 (C), 42.8 (CH_2), 64.6 (C), 127.9 (CH), 128.5 (2×CH), 129.6 (2×CH), 138.1 (C), 175.9 (C); MS: 208 (2), 172 (2), 166 (6), 164 (25), 163 (12), 162 (17), 149 (7), 131 (4), 130 (12), 129 (100), 128 (75), 127 (42), 115 (14), 103 (10), 102 (20), 101 (6). The compound as obtained was not sufficiently pure for elemental analysis.

1,1-Dibromo-2-bromomethyl-2-phenylcyclopropane (**7**).[15] ^1H NMR: δ 1.94 (1 H, d, *J* 8.02 Hz), 2.19 (1 H, dd, *J* 1.52 and 8.02 Hz), 3.77 (1 H, d, *J* 10.47 Hz), 3.90 (1 H, dd, *J* 1.52 and 10.47 Hz), 7.3 (5 H, m); ^{13}C NMR (125.759 MHz): δ 34.6, 34.7, 40.0, 42.5, 128.2, 128.3, 129.7, 138.1.

2-Bromomethyl-1,1-dichloro-2-phenylcyclopropane (**8**).[15] ^1H NMR: δ 1.85 (1 H, d, *J* 7.68 Hz), 2.08 (1 H, dd, *J* 1.41 and 7.68 Hz), 3.81 (1 H, d, *J* 10.57 Hz), 3.91 (1 H, dd, *J* 1.41 and 10.57 Hz), 7.33–7.42 (5 H, m).

2,2-Dibromo-2-phenylcyclopropylmethanol (**9**).[16] ^1H NMR: δ 1.77 (1 H, dd, *J* 5.63 and 8.46 Hz, OH), 2.05 (1 H, d, *J* 7.67 Hz), 2.10 (1 H, dd, *J* 0.61 and 7.67 Hz), 3.95 (1 H, dd, *J* 8.46 and 11.96), 4.05 [1 H, ddd, *J* 0.61 (barely visible), 5.63 and 11.96 Hz], 7.33–7.41 (5 H, m); ^{13}C NMR: δ 31.8, 32.5, 41.0, 70.2, 128.0, 128.5, 129.7, 138.5.

2,2-Dichloro-1-phenylcyclopropylmethanol (**10**).[15] ^1H NMR: δ 1.72 (1 H, broad s, OH), 1.87 (1 H, d, *J* 7.35 Hz), 1.92 (1 H, dd, *J* 0.66 and 7.35 Hz), 3.94 (1 H, broad d, *J* 11.75 Hz), 4.01 (1 H, d, *J* 11.75 Hz), 7.26 (1 H, s), 7.32–7.41 (5 H, m).

1,1-Dibromo-2-phenyl-2-propylcyclopropane (**11**) was isolated as an oil in 77 % (1.39 g) yield by hydrogenation (1 atm) of **1** (1.80 g, 5.7 mmol), using ethanol and acetic acid (6:1) as solvent.[17] IR(film): 3060 (w), 3020 (w), 2950 (s), 2930 (s), 2870 (m), 1600 (w), 1495 (m), 1465 (m), 1445 (s), 1427 (m), 1380 (w), 1090 (m), 1050 (m), 1020 (m), 765 (s), 695 (s) cm^{-1}; ^1H NMR: δ 0.84 (3 H, t, *J* 7.37 Hz), 1.20–1.28 (2 H, m), 1.68 (1 H, eight-line m), 1.76 (1 H, d, *J* 7.46 Hz), 2.08 (1 H, dd, *J* 1.54 and 7.46 Hz), 2.19 (1 H, 15-line m), 7.25–7.38 (5 H, m); ^{13}C NMR: δ 13.9 (CH_3), 20.4 (CH_2), 33,2 (CH_2), 36.6 (C), 40.0 (C), 42.6 (CH_2), 127.2 (CH), 128.1 (2×CH), 129.3 (2×CH), 140.7 (C); MS (2, M^+), 318 (3, M^+), 316 (1, M^+), 277 (13), 275 (27), 273 (14), 240 (24), 239 (85), 238 (30), 237 (86), 198 (18), 197 (85), 196 (41), 195 (92), 194 (24), 193 (66), 158 (31), 157 (77), 143 (19), 142 (36), 141 (31), 132 (24), 131 (50), 130 (49), 129 (92), 128 (86), 127 (49), 117 (89), 116 (90), 115 (100), 103 (66), 91 (82), 77 (80); mol. wt., obs. 319.927 866, calc. for $C_{12}H_{14}Br_2$ 319.942 131.

1,1-Dichloro-2-phenyl-2-propylcyclopropane (**12**) was isolated as an oil in 73 % (2.02 g) yield by hydrogenation (1 atm) of **2** (2.76 g, 12.1 mmol), using ethanol and acetic acid (6:1) as solvent.[17] IR (film): 3060 (w), 3020 (w), 2950 (s), 2930 (s), 2860 (m), 1600 (w), 1495 (m), 1465 (m), 1445 (s), 1420 (w), 1380 (w), 1098 (m), 1078 (m), 1045 (m), 1025 (m), 775 (s), 755 (s), 695 (s) cm^{-1}; ^1H NMR: δ 0.69–0.86 (3 H, m), 1.09–1.19 (2 H, m), 1.46 (1 H, d, *J* 7.13 Hz), 1.54–1.60 (1 H, m), 1.76 (1 H, dd, *J* 1.47 and 7.13 Hz), 1.93–2.03 (1 H, m), 7.19–7.26 (5 H, m); ^{13}C NMR: δ 13.9, 20.2, 31.7, 40.5, 41.0, 66.0, 127.2, 128.2, 129.5, 139.7; MS: 232 (6, M^+), 230 (36, M^+), 228 (51, M^+), 196 (3), 195 (24), 194 (11), 193 (60), 189 (6), 187 (40), 185 (59), 165 (18), 163 (49), 157 (30), 153 (32), 151 (97), 149 (95), 129 (60), 128 (59), 117 (98), 115 (100), 103 (45), 91 (62), 77 (56); mol. wt., obs. 232.020 798, calc. for $C_{12}H_{14}Cl_2$ 232.041 356.

2,2-Dichloro-1-phenylcyclopropylmethyl p-*nitrobenzoate* (**13**). A solution of 2.14 g (9.9 mmol) of **10** and 1.84 g (9.9 mmol) of *p*-nitrobenzoyl chloride in benzene (10 ml) was refluxed for 1 h. Evaporation of the solvent left a residue which was dissolved in ether and subsequently washed with water. A pure sample of the product (0.74 g, 20 %) was isolated by column chromatography on SiO_2; unreacted acid chloride was removed by benzene and pure **13** was obtained using pentane; m.p. 124–130 °C. IR (KBr): 3090 (w), 3070 (w), 2950 (w), 2860 (w), 1723 (s), 1600 (m), 1518 (s), 1442 (m), 1340 (s), 1320 (m), 1260 (s), 1230 (m), 1115 (s), 1100 (s), 1060 (m), 1035 (m), 1010 (m), 975 (m), 930 (w), 865 (m), 835 (m), 778 (s), 705 (s) cm^{-1}; ^1H NMR: δ 2.02 (1 H, d, *J* 7.55 Hz), 2.07 (1 H, dd, *J* 0.56 and 7.55 Hz), 4.69 (1 H, dd, *J* 0.56 and 11.63 Hz), 4.79 (1 H, d, *J* 11.63 Hz), 7.31–7.47 (5 H, m), 8.09–8.31 (4 H, m); ^{13}C NMR: δ 31.0, 39.1, 63.4, 70.5, 123.6, 128.2, 128.6, 129.8, 130.7, 135.2, 136.8, 150.8, 164.1; MS: 232 (6), 230 (30), 228 (45), 195 (20), 193 (59), 187 (34), 185 (53), 165 (11), 163 (36), 157 (22), 153 (27), 151 (100), 150 (18), 149 (81), 129 (47), 128 (42), 117 (89), 115 (88), 103 (30), 91 (41), 77 (35). Anal. $C_{17}H_{13}Cl_2NO_4$: C, H.

2,2-Dibromo-1-propylcyclopropanecarboxylic acid (**14**) was prepared from **11** (970 mg, 3.1 mmol) using ruthenium tetroxide as described in the literature.[18] After five days, extraction with ether and isolation of the acidic material in the usual way afforded 385 mg of recovered starting material and 299 mg (58 % based on consumed **11**) of **14** as an

oil. IR (CCl_4): 3300–2400 (s), 2960 (s), 2920 (s), 2860 (m), 1705 (s), 1440 (m), 1410 (m), 1230 (m), 1025 (m), 903 (m), 687 (m) cm^{-1}; ^1H NMR: δ 0.89 (3 H, m, almost a t), 1.3–1.6 (2 H, m), 1.53 (1 H, d, *J* 7.93 Hz), 1.98–2.15 (1 H, m), 2.29 (1 H, dd, *J* 1.34 and 7.93 Hz), 2.34–2.41 (1 H, m), 9.72 (1 H, br s); ^{13}C NMR: δ 13.8, 20.3, 28.4, 31.6, 36.9, 39.6, 175.0; MS: 288 (2, M^+), 286 (3, M^+), 284 (2, M^+), 259 (27), 257 (52), 255 (28), 243 (2), 242 (3), 241 (4), 207 (82), 205 (90), 201 (26), 188 (27), 186 (53), 184 (28), 179 (38), 177 (54), 149 (59), 147 (60), 135 (42), 133 (40), 125 (62), 119 (36), 100 (77), 97 (100), 81 (88); mol. wt., obs. 287.943 550; calc. for $C_7H_{10}Br_2O_2$ 287.900 660.

2,2-Dichloro-1-propylcyclopropanecarboxylic acid (**15**) was prepared from **12** (700 mg, 3.0 mmol) using ruthenium tetroxide as described in the literature.[18] After two days, extraction with ether and isolation of the acidic material in the usual way afforded 510 mg of recovered starting material and 100 mg (63 % based on consumed **12**) of **15** as an oil. IR (CCl_4): 3300–2400 (s), 2960 (s), 2920 (s), 2860 (m), 1705 (s), 1440 (m), 1410 (m), 1235 (m), 1053 (m), 903 (m) cm^{-1}; ^1H NMR: δ 0.95 (3 H, m, almost a t), 1.3–1.6 (3 H, m), 1.46 (1 H, d, *J* 7.62 Hz), 2.23 (1 H, dd, *J* 1.15 and 7.62 Hz), 2.35–2.43 (1 H, m), 11.7 (1 H, br s); ^{13}C NMR: δ 13.8, 20.3, 29.8, 34.4, 62.0, 174.6; MS: 200 (2, M^+), 198 (8, M^+), 196 (13, M^+), 171 (10), 169 (59), 167 (87), 155 (2), 153 (4), 151 (7), 133 (17), 131 (38), 111 (23), 109 (34), 104 (37), 103 (100), 97 (47), 87 (15), 82 (25); mol. wt., obs. 200.021 103, calc. for $C_7H_{10}Cl_2O_2$ 199.999 885.

^1H NMR spectroscopy. The spectra were recorded in ordinary 5 mm tubes using samples that were some 5 % by weight in deuteriochloroform ($CDCl_3$). The solvent provided the deuterium resonance for the NMR field lock. Oxygen was not removed from the samples. The spectra of the acids (**4**, **5**, **6**, **14** and **15**) were observed over a range of 6000 Hz, those of the other compounds over a range of 5000 Hz. NOE difference measurements were carried out by recycling a frequency list using a preirradiation time of 5 s, which is much longer than the expected T_1 values for the proton studied here. The saturation obtained was close to 100 %.

Variable-temperature studies were carried out with dibromides **1** and **5** under the conditions described above, except that toluene-d_8 was used as solvent. Spectra were run at every 20 K from 300 to 400 K for **1** and at every 10 K from 300 and 390 K for **5**. Increasing temperature did not change J_{A4} for **5**; for **1**, however, J_{A4} diminished as follows: 1.22 Hz at 300 K, 1.22 Hz at 320 K, 1.22 Hz at 340 K, 1.22 Hz at 360 K, 1.10 Hz at 380 K, and 0.99 Hz at 400 K.

X-Ray crystallography. Satisfactory crystals of *gem*-dihalocyclopropanes **5**, **6** and **8** were prepared by recrystallization from hexane, whereas crystals of **13** were obtained by re-

Table 1. Crystal and experimental data for 2-(2,2-dibromo-1-phenylcyclopropyl)ethanoic acid ($C_{11}H_{10}Br_2O_2$) (**5**), 2-(2,2-dichloro-1-phenylcyclopropyl)ethanoic acid ($C_{11}H_{10}Cl_2O_2$) (**6**), 2-bromomethyl-1,1-dichloro-2-phenylcyclopropane ($C_{10}H_9BrCl_2$) (**8**) and 2,2-dichloro-1-phenyl-cyclopropylmethyl 4-nitrobenzoate ($C_{17}H_{13}Cl_2NO_4$) (**13**).

Compound	$C_{10}H_{11}Br_2O_2$	$C_{10}H_{11}Cl_2O_2$	$C_{10}H_9BrCl_2$	$C_{17}H_{13}Cl_2NO_4$
Melting point				
Diffractometer	Syntex *P* 1	Nicolet *P* 3/*F*	Nicolet *P* 3/*F*	Nicolet *P* 3/*F*
Crystal size/mm	0.3×0.4×0.5	0.2×0.3×0.4	0.3×0.3×0.5	0.3×0.3×0.2
Radiation, Mo*K*α (λ = 0.710 69 Å)				
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
a/Å	8.082(1)	8.129(1)	9.263(2)	6.210(1)
b/Å	15.591(2)	14.956(3)	11.423(2)	28.886(9)
c/Å	18.264(3)	18.431(4)	20.091(3)	9.022(3)
v/Å^3	2301.4(6)	2240.8(6)	2125.7(6)	1605.6(9)
T/°C	−140	−135	−135	−135
Space group	*Pbca*	*Pbca*	*Pbca*	$P2_1/n$
M	318.01	245.11	279.99	366.20
Z	8	8	8	4
F(000)	1296	1008	1104	736
D_x/g cm^{-3}	1.836	1.453	1.750	1.515
μ (Mo*K*α)/cm^{-1}	69.5	5.6	42.9	4.2
Scan mode	ω/2θ	ω/2θ	ω/2θ	ω
Scan speed/°min^{-1}	4	3	2–4	2–4
Scan range/°	2.0	1.7	2.1	1.9
Maximum sin θ/λ /Å^{-1}	0.9	0.8	0.8	0.76
No. of independent measurements with $I>3.0\sigma(I)$	2445	2780	3048	3324
Correction for absorption	Empirical	Empirical	Empirical	Empirical
No. of parameters refined	176	176	154	308
$R=\Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.051	0.052	0.048	0.042
$R_w[\Sigma w(F_o-F_c)^2/\Sigma wF_o^2]^{1/2}$	0.037	0.047	0.050	0.045
$S=[\Sigma w(F_o-F_c)^2/(n-m)]^{1/2}$	2.65	1.52	1.81	1.06

Table 2. Fractional atomic coordinates and U_{eq} [= (1/3) ΣU_{ij}] for **5**, **6**, **8** and **13**.

Atom	*x*	*y*	*z*	U_{eq}
$C_{11}H_{10}Br_2O_2$				
Br1	0.70691(6)	0.14321(3)	0.11535(3)	0.019
Br2	0.37071(6)	0.23438(3)	0.15901(3)	0.021
O1	1.0675(4)	0.4233(2)	0.0701(2)	0.020
O2	0.8290(4)	0.4465(2)	0.0121(2)	0.018
C1	0.5773(5)	0.2458(3)	0.1070(2)	0.014
C2	0.6567(5)	0.3323(3)	0.1028(2)	0.009
C3	0.5762(6)	0.2923(3)	0.0359(2)	0.015
C4	0.8443(5)	0.3367(3)	0.1038(2)	0.010
C5	0.9103(5)	0.4085(3)	0.0573(2)	0.011
C6	0.5755(5)	0.4076(3)	0.1388(2)	0.009
C7	0.4758(5)	0.4645(3)	0.0993(2)	0.012
C8	0.4089(5)	0.5353(3)	0.1326(2)	0.013
C9	0.4380(6)	0.5514(3)	0.2064(3)	0.016
C10	0.5356(5)	0.4961(3)	0.2455(3)	0.015
C11	0.6035(5)	0.4247(3)	0.2131(2)	0.012
$C_{11}H_{10}Cl_2O_2$				
Cl1	0.68225(9)	0.14390(3)	0.11433(4)	0.039
Cl2	0.37926(8)	0.23493(4)	0.15342(4)	0.042
O1	1.0650(2)	0.4208(1)	0.0709(1)	0.036
O2	0.8291(2)	0.4462(1)	0.0122(1)	0.033
C1	0.5661(3)	0.2425(1)	0.1065(1)	0.031
C2	0.6517(2)	0.3324(1)	0.1030(1)	0.024
C3	0.5709(3)	0.2919(1)	0.0364(1)	0.032
C4	0.8381(2)	0.3335(1)	0.1056(1)	0.027
C5	0.9084(2)	0.4064(1)	0.0578(1)	0.025
C6	0.5724(2)	0.4110(1)	0.1393(1)	0.024
C7	0.4722(3)	0.4702(1)	0.1009(1)	0.028
C8	0.4082(3)	0.5452(2)	0.1341(1)	0.032
C9	0.4395(3)	0.5619(1)	0.2067(1)	0.033
C10	0.5357(3)	0.5027(2)	0.2461(1)	0.033
C11	0.6028(3)	0.4276(1)	0.2127(1)	0.029
$C_{10}H_9BrCl_2$				
Br1	0.46183(4)	0.08442(3)	0.24707(1)	0.029
Cl1	0.78699(8)	−0.22363(7)	0.33254(4)	0.029
Cl2	0.61127(9)	−0.24047(7)	0.45062(4)	0.030
C1	0.6585(3)	−0.1517(3)	0.3828(2)	0.024
C2	0.5474(3)	−0.0727(2)	0.3514(1)	0.021
C3	0.6685(4)	−0.0224(3)	0.3926(2)	0.025
C4	0.5572(4)	−0.0592(3)	0.2767(2)	0.024
C5	0.3951(3)	−0.0744(3)	0.3777(1)	0.022
C6	0.3036(3)	−0.1659(3)	0.3616(2)	0.025
C7	0.1593(3)	−0.1625(3)	0.3808(2)	0.028
C8	0.1064(4)	−0.0686(3)	0.4158(2)	0.033
C9	0.1990(4)	0.0236(3)	0.4335(2)	0.034
C10	0.3425(4)	0.0196(3)	0.4143(2)	0.029
$C_{17}H_{13}Cl_2NO_4$				
Cl1	0.36599(11)	0.19075(2)	0.06235(7)	0.027
Cl2	0.52404(12)	0.23898(2)	0.33536(8)	0.035
O1	0.4301(3)	0.1436(1)	0.5260(2)	0.026
O2	0.4965(3)	0.1739(1)	0.7561(2)	0.031
O3	1.4524(4)	0.0470(1)	0.8390(3)	0.042
O4	1.3553(4)	0.0142(1)	0.6259(3)	0.043
N1	1.3253(4)	0.0416(1)	0.7250(3)	0.029
C1	0.3085(4)	0.2066(1)	0.2409(3)	0.024
C2	0.1800(4)	0.1739(1)	0.3271(3)	0.022
C3	0.0829(4)	0.2190(1)	0.2631(3)	0.027
C4	0.2391(4)	0.1729(1)	0.4947(3)	0.026
C5	0.0986(4)	0.1291(1)	0.2574(3)	0.021
C6	0.2374(4)	0.0915(1)	0.2495(3)	0.025
C7	0.1599(5)	0.0496(1)	0.1893(3)	0.031
C8	−0.0582(5)	0.0448(1)	0.1355(3)	0.032
C9	−0.1978(5)	0.0818(1)	0.1424(3)	0.031
C10	−0.1201(4)	0.1236(1)	0.2041(3)	0.026
C11	0.5472(4)	0.1487(1)	0.6598(3)	0.023
C12	0.7483(4)	0.1200(1)	0.6741(3)	0.023
C13	0.9012(5)	0.1266(1)	0.7992(3)	0.027
C14	1.0903(5)	0.1009(1)	0.8165(3)	0.026
C15	1.1232(4)	0.0690(1)	0.7069(3)	0.024
C16	0.9749(5)	0.0620(1)	0.5811(3)	0.026
C17	0.7854(4)	0.0875(1)	0.5661(3)	0.025

crystallization from diethyl ether. Data for unit-cell determination and intensity data for structure determination were collected using four-circle diffractometers with graphite-crystal monochromated Mo*K*α radiation (λ = 0.71069 Å) at low temperatures. Experimental and crystal data are given in Table 1.

The atomic coordinates of all the non-hydrogen atoms were determined by direct methods (MITHRIL)[19] for **5**, **8** and **13**. Compounds **5** and **6** are isomorphous and the parameters obtained for **5** could thus be used directly as starting parameters for the refinement of **6**. All refinements were performed by least-squares calculations; the hydrogen positions were found from difference Fourier syntheses and were included in the least-squares calculations. An empirical absorption correction was applied to the four data sets.[20] Computer programs applied are described in Ref. 21. Final figures of merit are included in Table 1. Positional parameters for non-hydrogen atoms are given in Table 2. Lists of hydrogen coordinates, anisotropic thermal parameters and structure factors may be obtained from the authors on request.

Selected bond lengths, bond angles and torsion angles for all the compounds are compiled in Table 3. ORTEP drawings of compounds **6**, **8** and **13** are shown in Fig. 1.

Computations. Semiempirical calculations were carried out on 1,1-dibromo-2-ethyl-2-phenylcyclopropane (**16**), a model compound for cyclopropanes **1–13**, and 1-ethyl-1-phenylcyclopropane (**17**). The computations were performed using the AM1 method[22] available in the MOPAC (v4.00) program.[23] Input to MOPAC was made by using INSIGHT from Biosym Technologies. Both programs were run on a Silicon Graphics IRIS 4D/70GT work station. All torsional forcing was carried out using the method of adiabatic mapping, making an optimization of all optimizable coordinates at every step. In the exploratory calculations the minimization routine was often trapped in local energy minima. This was avoided in subsequent calculations by

Table 3. Selected bond lengths (in Å), bond angles (in °) and torsion angles (in °).[a]

				$C_{11}H_{10}Br_2O_2$	$C_{11}H_{10}Cl_2O_2$	$C_{10}H_9BrCl_2$	$C_{17}H_{13}Cl_2NO_4$
Distances							
X1	C1			1.918(5)	1.757(2)	1.765(4)	1.754(3)
X2	C1			1.929(5)	1.751(2)	1.753(4)	1.763(3)
Br1	C4					1.956(4)	
C1	C2			1.495(3)	1.515(3)	1.507(5)	1.512(4)
C1	C3			1.487(6)	1.489(3)	1.493(5)	1.483(4)
C2	C3			1.518(6)	1.519(3)	1.509(5)	1.520(4)
C2	C4			1.518(6)	1.516(3)	1.511(4)	1.512(4)
C4	C5			1.502(6)	1.513(2)		
C5	O1			1.312(6)	1.313(3)		
C5	O2			1.210(6)	1.216(3)		
O1	O2			2.660(6)	2.654(2)		
C2	C5					1.507(4)	1.499(4)
C2	C6			1.497(6)	1.499(3)		
C4	O1						1.456(4)
O1	C11						1.337(3)
C11	C12						1.491(4)
C11	O2						1.205(4)
H31	H41			3.72	3.64	3.50	3.71
H32	H41			2.58	2.58	2.46	3.08
H31	H42			3.59	3.66	3.52	3.55
H32	H42			>4.0	>4.0	>4.0	2.41
Angles							
X1	C1	C2		121.4(3)	120.1(2)	119.9(3)	119.4(2)
X1	C1	C3		118.6(3)	118.3(2)	119.6(3)	119.4(2)
X2	C1	C2		118.7(3)	118.5(2)	120.1(3)	120.0(2)
X2	C1	C3		118.0(4)	118.9(2)	119.1(3)	118.6(2)
X1	C1	X2		110.6(3)	111.8(1)	110.1(2)	110.6(2)
C2	C1	C3		61.2(3)	60.7(1)	60.4(2)	61.0(2)
C1	C2	C3		59.1(3)	58.8(1)	59.4(2)	58.6(2)
C1	C3	C2		59.7(3)	60.5(1)	60.3(2)	60.4(2)
C1	C2	C4		118.0(4)	117.5(2)	115.9(3)	116.6(3)
C3	C2	C4		117.1(4)	117.5(2)	117.5(3)	115.6(3)
C1	C2	C6		119.8(4)	118.7(2)		
C1	C2	C5				119.0(3)	119.7(2)
C3	C2	C6		119.2(4)	119.2(2)		
C3	C2	C5				120.6(3)	119.0(3)
C4	C2	C6		113.4(4)	114.0(2)		
C4	C2	C5				113.9(3)	115.5(2)
C2	C4	C5		112.4(4)	111.6(2)		
C4	C5	O1		112.0(4)	112.2(2)		
C4	C5	O2		123.0(4)	123.7(2)		
O1	C5	O2		124.1(4)	124.1(2)		
C2	C4	Br1				111.1(3)	
C2	C4	O1					107.2(2)
Torsion angles							
H31	C3	C2	C4	138	148	149	145
H32	C3	C2	C4	1	−2	6	1
C3	C2	C4	H41	47	46	26	−95
C3	C2	C4	H42	163	166	150	28
C3	C2	C4	C5	−78	−77		
C3	C2	C4	Br1			−91	
C3	C2	C4	O1				147
C1	C2	C4	C5	146	144		
C1	C2	C4	Br1			−157	
C1	C2	C4	O1				81
C3	C2	C6	C7	28	27		
C3	C2	C5	C10			39	37
C3	C2	C4	O1				147

[a]Estimated standard deviations are calculated from the variance-covariance matrix. Cyclopropane halogen atoms are denoted by X. For numbering of atoms, see Fig. 1.

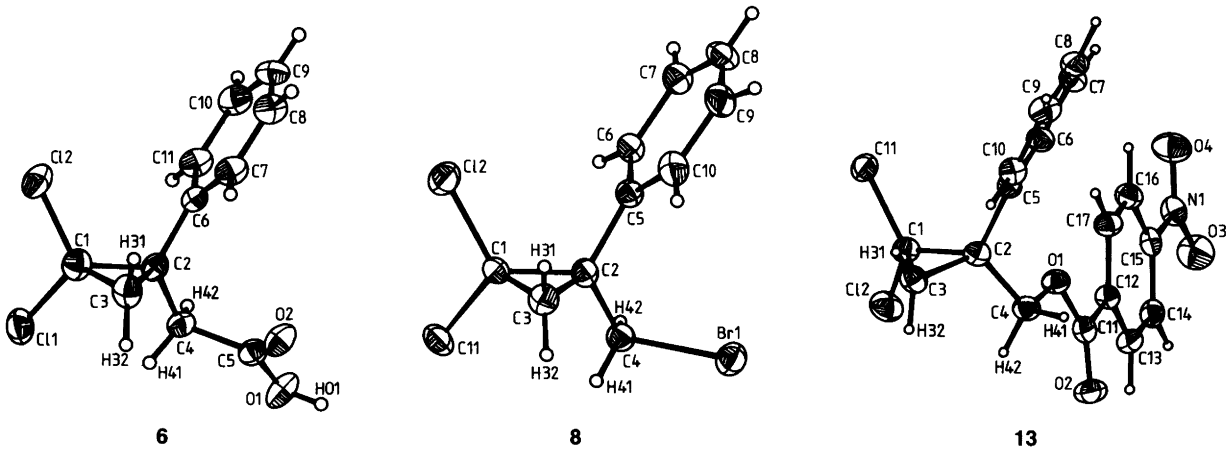

Fig. 1. ORTEP plots of the structures of 2-(2,2-dichloro-1-phenylcyclopropyl)ethanoic acid (**6**), 2-bromomethyl-1,1-dichloro-2-phenylcyclopropane (**8**) and 2,2-dichloro-1-phenylcyclopropylmethyl 4-nitrobenzoate (**13**). Dibromide **5** is isomorphous with dichloride **6**.

employing the PRECISE keyword, which increased the criteria for terminating the optimizations by a factor of 100.

Grid mapping was performed for simultaneous rotation of the phenyl and ethyl groups for both compounds. With 11 steps for each rotation a total of 121 data points were collected. The step size was 36° for the ethyl group; for the phenyl group the size was 18° owing to the symmetry of the ring. In addition a torsional forcing of the ethyl substituent, with free rotation of the phenyl group, was carried out; a total of 44 and 57 data points were collected for **16** and **17**, respectively.

Results

NMR spectroscopy. A large number of cyclopropanes containing a methylene group next to the ring were synthesized using well established procedures. The proton NMR spectra were subsequently recorded with high resolution (better than 0.25 Hz) in order to detect spin–spin coupling between the cyclopropyl protons and the methylene protons next to the ring. Many of the compounds examined gave spectra that did not show any sign of such interactions, but the spectra of some of 2-substituted, 1,1-dihalo-2-phenylcyclopropanes (**2–13**), of 2,2-dibromo-1-propylcyclopropanecarboxylic acid (**14**), and of 2,2-dichloro-1-propylcyclopropanecarboxylic acid (**13**), synthesized as described in the experimental section, exhibited the four-bond coupling under consideration.

All the spectra were unambiguously assigned by a combination of decoupling, NOE and COSY experiments. The presence of the long-range coupling is generally most clearly visible in those parts of the spectra associated with the protons attached to the ring, *i.e.* H_A and H_B (Scheme 1). For all compounds one of these protons gives rise to a doublet and the other proton to a double doublet, of which the former consistently appears at the higher field (Table 4). On the basis of the field anisotropy around the phenyl (compounds **2–13**) and carboxyl (acids **14** and **15**) groups[24] and by analogy with the spectrum of compound **1**[9] it seems most likely that H_A, and not H_B, is involved in coupling outside the ring and thus appears at the lower field. This conclusion was supported by successful NOE investigations of compounds **6** and **10**. Thus, when the methylene protons next to the three-membered ring, *i.e.* H41 and H42 (Scheme 1), were irradiated, enhancement of the intensity of the doublet but *not* of the double doublet was observed. Furthermore, for all the compounds enhancement of the signals due to H41 and H42 was observed only when the cyclopropyl proton associated with the doublet was irradiated. It is therefore concluded that the long-range coupling observed for compounds **2–15** is between the cyclopropyl proton situated *trans* to the methylene group next to the

Table 4. Chemical shifts for the cyclopropyl protons and the methylene protons next to the cyclopropane ring for compounds **1–15** (for notation, see Scheme 1).

Compound	δ_{H42}/ppm	δ_{H41}/ppm	δ_{H_A}/ppm[a]	δ_{H_B}/ppm[b]
1[c]	2.92	2.49	2.08	1.79
2	2.87	2.50	1.90	1.64
3	2.21	1.85	2.10	1.78
4	2.39	2.07	2.02	1.77
5	3.25	2.92	2.29	2.05
6	3.18	2.88	2.11	1.88
7	3.90	3.77	2.19	1.94
8	3.91	3.81	2.08	1.85
9	4.05	3.95	2.10	2.05
10	3.94	4.01	1.92	1.87
11	2.17	1.68	2.08	1.76
12	1.98	1.57	1.76	1.46
13	4.69	4.79	2.07	2.02
14	2.37	2.06	2.29	1.53
15	2.39	1.5[d]	2.23	1.46

[a]Appears as a double doublet. [b]Appears as a doublet. [c]Taken from Ref. 9. [d]This proton overlaps with the other methylene protons of the propyl group and the chemical shift is therefore difficult to determine.

Table 5. Absolute values of the geminal (J_{AB}) and long-range (J_{A4}) proton–proton coupling constants, measured at 500.1 MHz, involving the ring protons of cyclopropanes **1–15**. $CDCl_3$ was used as solvent.

Compound	X	R^1	R^2	J_{AB}/Hz	J_{A4}/Hz
1[a]	Br	Ph	$CH{=}CH_2$	7.64	1.40
2	Cl	Ph	$CH{=}CH_2$	7.28	1.28
3	Br	Ph	CH_2CH_2OH	7.52	1.50
4	Br	Ph	CH_2COOH	7.62	1.42
5	Br	Ph	COOH	8.29	1.40
6	Cl	Ph	COOH	7.94	1.31
7	Br	Ph	Br	8.02	1.52
8	Cl	Ph	Br	7.68	1.41
9	Br	Ph	OH	7.67	0.61
10	Cl	Ph	OH	7.35	0.66
11	Br	Ph	CH_2CH_3	7.46	1.54
12	Cl	Ph	CH_2CH_3	7.13	1.47
13	Cl	Ph	$OOCC_6H_4NO_2$	7.55	0.56
14	Br	COOH	CH_2CH_3	7.93	1.32
15	Cl	COOH	CH_2CH_3	7.62	1.15

[a]Taken from Ref. 9.

cyclopropane ring, *i.e.* H_A, and either H41 or H42 (H4 used as common notation). Consequently, the nature of this long-range coupling is identical to that previously found for 1,1-dibromo-2-phenyl-2-(2-propenyl)cyclopropane.[9]

The values of the geminal and the long-range coupling constants involving H_A, denoted J_{AB} and J_{A4}, respectively, are summarized in Table 5 for all compounds. These data clearly show that both coupling constants are sensitive to the nature of the halogen atom attached to the ring; thus the absolute values of J_{AB} and J_{A4} are generally larger for the *gem*-dibromocyclopropanes than for the corresponding *gem*-dichlorocyclopropanes, *e.g.* dibromides **1** and **5** as compared to dichlorides **2** and **6**, respectively (Table 5). It is also evident that within each group of halocyclopropanes the geminal coupling constant, which conceivably is negative,[25–27] is rather insensitive to the electron-withdrawing properties of R^2. The variation of J_{AB} is therefore much smaller than when R^2 is directly attached to the cyclopropane ring, in which case electronegative substituents generally affect geminal interproton coupling within the ring to a considerable extent.[28] The long-range coupling constant J_{A4}, on the other hand, varies over a relatively large range when R^2 is altered, from 0.56 to 1.47 Hz for the *gem*-dichlorocyclopropanes and from 0.61 to 1.54 Hz for the *gem*-dibromocyclopropanes (Table 5). Whether this coupling is based on σ–σ or σ–π interactions or both is unknown,[6,7,29,30] but whatever the coupling mechanism, theory, which is supported by many observations, predicts that J_{A4} can be influenced by electronic as well as conformational effects.[31] However, if electronic effects were significant, J_{A4} for dibromides like **4** (R^2 = CH_2COOH), **5** (R^2 = COOH), **7** (R^2 = Br) and **11** (R^2 = CH_2CH_3) should be rather different, as should J_{A4} for dichlorides like **6** (R^2 = COOH), **8** (R^2 = Br) and **12** (R^2 = CH_2CH_3), but this is not the case (Table 5). We therefore assume that different values of J_{A4} for compounds within each group of *gem*-dihalocyclopropanes first and foremost arise because of conformational differences between the molecules.

Coupling constants that are sensitive to conformational changes may be different for two molecules either because the molecules in solution exist in two different and almost fixed conformations or because conversion between rotamers in solution occurs rapidly (on the NMR timescale) and in such a way that the average conformation of each molecule is different. In order to find out which explanation is the more plausible one for cyclopropanes **1–15** we decided to perform a crystal structure determination of all the compounds that gave samples suitable for X-ray diffraction studies. As it turned out, four of the substances, *viz.* 2-(2,2-dibromo-1-phenylcyclopropyl)ethanoic acid (**5**), 2-2,2-dichloro-1-phenylcyclopropyl)ethanoic aicd (**6**), 2-bromomethyl-1,1-dichloro-2-phenylcyclopropane (**8**) and 2,2-dichloro-1-phenylcyclopropylmethyl 4-nitrobenzoate (**13**), in addition to **1**,[9] gave crystals of the quality required. When their structures were determined (*vide supra*) and plotted (Fig. 1) it was apparent that the rotation of the CH_2R^2 moiety about the C2–C4 bond was different for all the compounds, but in particular for compound **13** as compared to **5**, **6** and **8**. Thus, the latter group of compounds exhibited *anti* conformations about the C2–C4 bond, acids **5** and **6** *ac* and bromide **8** *ap*, as does **1**,[9] whereas ester **13** attains a *syn* conformation (*sc*) (Fig. 1 and Table 3). The solid-state conformation about the C2–C4 bond of compound **13** is therefore significantly different from those of compounds **1**, **5**, **6** and **8**. On the assumption that the conformations in the solid state and in solution are similar we would expect to find that compound **13** has a considerably different J_{A4} as compared to compounds **1**, **5**, **6** and **8**, and this was in fact observed; the average value for J_{A4} for the latter group of cyclopropanes is 1.38 Hz, whereas the value is 0.56 Hz for the dichloride **13**.

As mentioned previously, enhancement of the signals due to H41 and H42 was observed when NOE experiments were carried out with irradiation of H_B. However, these signals were not enhanced to the same extent in a single case. In all successful experiments but two the signals due to the proton *not* involved in observable coupling to H_A were enhanced by far the most. This means that H_A in compounds **5**, **6** and **8** are coupled to H42 (Fig. 1), which conceivably is the case for most of the other compounds as well. The two exceptions are the dichlorides **10** and **13**, for which no safe conclusion can be drawn on the basis of the NOE experiments because the enhancements of the H41 and H42 signals were rather similar when H_B was irradiated, and essentially absent when H_A was irradiated. If the crystal structures depicted in Fig. 1 are close to the predominant structures of the same molecules in solution, these NOE results are reasonable. Consequently, the NOE experiments lend support to the assumption that the average conformations in solution and in the solid state are similar.

Several theoretical descriptions of long-range coupling over four bonds (^4J) exist in the literature.[31,32] In a previous

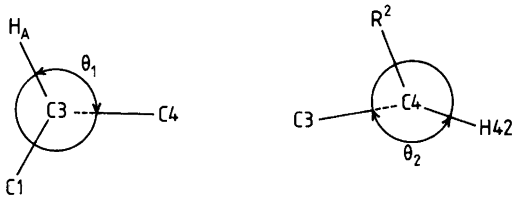

Fig. 2. The torsional angles θ_1 and θ_2 in the H–C–C–C–H fragment involved in long-range coupling. For notation, see Scheme 1 and Fig. 1.

paper[9] we employed the empirical equations developed by Bystrov and Stephanyants[33] to calculate J_{A4} for **1** in solution on the basis the torsional angles θ_1 and θ_2 (Fig. 2) obtained from its crystal structure. The agreement between calculated and observed J_{A4} values were reasonable in this case,[9] which indicates that the average conformation of **1** is similar in solution and in the solid state. When the same equations[33] are used to examine J_{A4} for compounds **5**, **6**, **8** and **13** similar agreements are apparent. Thus, the experimental long-range couplings are reasonably close to the ^4J values calculated for coupling between H_A and H42 for all these compounds, but very different from those calculated for analogous coupling between H_A and H41 (Table 6). These results clearly support the conclusion that H_A is coupled to H42 and *not* to H41.

Another interesting feature with the spectra, which is in accordance with the conclusions outlined above, is associated with the chemical shifts of the methylene protons next to the three-membered ring. These shifts are obtained for all compounds but one, *viz.* **14**, and in almost all cases H42, which is coupled to H_A, appears at a lower field than H41 (Table 4). The exceptions are the dichlorides **10** and **13**, which show coupling between H_A and the high-field proton attached to C4. The change in the relative chemical shifts for H41 and H42 for compounds **10** and **13** is conceivably related to conformational changes which change the positions of H41 and H42 in the fields surrounding the phenyl group and the cyclopropane ring. This explanation is supported by the different conformation about the C2–C4 bond in the crystal structure of **13** as compared to **5**, **6** and **8** (Fig. 1).

The results presented above suggest that the J_{A4} coupling depends mainly and intimately on the position of the C4–H42 bond relative to the cyclopropane ring. When the C3–C2 bond is essentially *anti* to the C4–H42 bond (conformer **a**, Fig. 3), as is the case for compounds **6** and **8** (Fig. 1), J_{A4} is much larger than when the same bonds are almost *syn* to each other (conformer **b**, Fig. 3), as in **13** (Fig. 1). Semiempirical calculations (*vide infra*) indicate that reversible interconversion between these two conformers requires addition of as little as 3–4 kcal mol^{-1}, and it is therefore reasonable to believe that a compound will exhibit a relatively large J_{A4} coupling when rotational equilibrium is reached with predominance of conformer **a**. Similarly, a relatively small J_{A4} coupling is observed when equilibrium is reached with predominance of conformer **b**. This suggests that a relatively large J_{A4} coupling is due to the fact that H31–C3–C2–C4–H42 in conformer **a** is the only system that approaches the well known zig-zag configuration of the W type, which is known to result in significant coupling in a large number of rigid molecules.[31,34,35] This configuration is not achieved to a comparable extent for the H31–C3–C2–C4–H41, H32–C3–C2–C4–H41 and H32–C3–C2–C4–H42 fragments in conformer **a** and not for any H–C–C–C–H system in conformer **b**. As a result the observed (averaged) J_{A4} coupling is much smaller when conformer **b** predominates, and, furthermore, no coupling (> 0.3 Hz) to H32 is detected.[31,32,36]

This explanation is supported by variable-temperature proton-NMR studies of 1,1-dibromo-2-phenyl-2-(2-propenyl)cyclopropane (**1**). In the crystal state (and conceivably also in solution) **1** exhibits a conformation that is close to that of conformer **a** and the J_{A4} coupling is therefore rather large (1.22 Hz). When the temperature is increased the amount of the less stable conformer **b**, for which J_{A4} is smaller, will increase, and J_{A4} should decrease, which is in fact observed; J_{A4} is 1.10 Hz at 380 K and 0.99 Hz at 400 K.

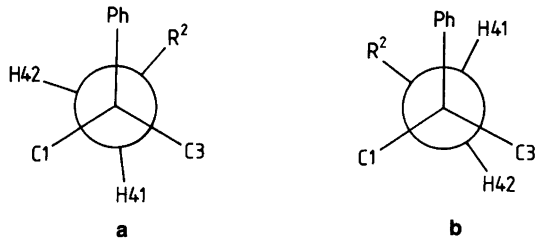

Fig. 3. Newman projection along the C2–C4 bond of two conformers, **a** and **b**, of cyclopropanes **1**–**13**.

Table 6. Torsional angles (θ_1 and θ_2), observed long-range coupling constants (J_{A4}) and calculated long-range coupling constants (^4J) for coupling of H_A to H41 and H42 in **5**, **6**, **8** and **13** (for notation, see Figs. 1 and 2).

Compound	θ_1/°	θ_2(H41)/°	θ_2(H42)/°	J_{A4}/Hz	^4J/Hz	
					H_A–H41	H_A–H42
5	138	47	163	1.40	−0.08	1.47
6	148	46	166	1.31	0.02	1.52
8	149	26	150	1.41	0.28	1.63
13	145	−95	28	0.56	1.48	0.21

The crystal structures. Compounds **5** and **6** are carboxylic acids and form, in keeping with expectations, hydrogen-bonded dimers at crystallographic centres of symmetry. The hydrogen bond lengths are 2.660 Å in the bromine compound and 2.654 Å in the chlorine analogue; these values are quite normal for hydrogen-bonded carboxylic acid dimers in the solid state.

The mean C–Br and C–Cl bond lengths are 1.924 and 1.757 Å, respectively, which are normal. The average C–C

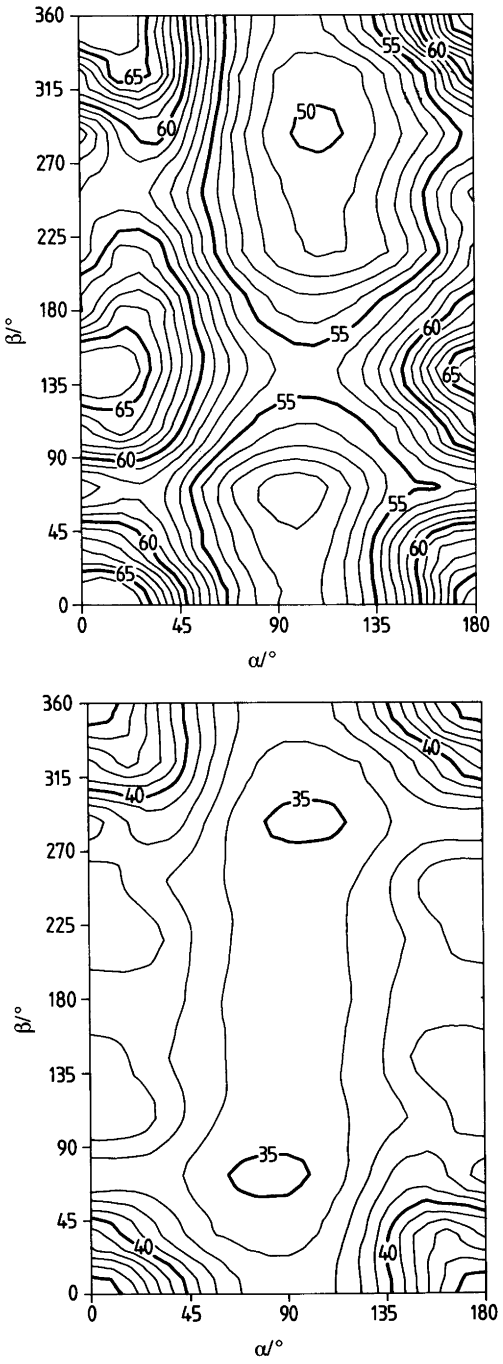

Fig. 4. The calculated (AM1) contour plot of the grid mapping over α and β for 1,1-dibromo-2-ethyl-2-phenylcyclopropane (**16**) (above) and 1-ethyl-1-phenylcyclopropane (**17**) (below).

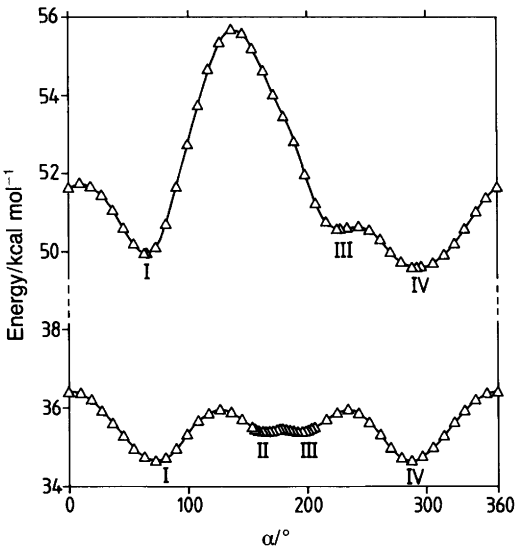

Fig. 5. Torsional forcing of β in 1,1-dibromo-2-ethyl-2-phenylcyclopropane (**16**) (upper curve) and 1-ethyl-1-phenylcyclopropane (**17**) (lower curve). The Roman numerals indicate energy minima.

bond length in the cyclopropane rings is also normal, ranging from 1.500 to 1.508 Å. As expected on the basis of the figures given by Allen,[37] the bond distal to the phenyl group is shortened by from 0.010 to 0.019 Å relative to the average bond length.

The intermolecular (**8** and **13**) and interdimer (**5** and **6**) separations are as expected from the sums of van der Waals radii.

In all the compounds the phenyl group attains a position relative to the cyclopropane ring that is much closer to a perpendicular than to a bisected conformation. This is not at all surprising, since the perpendicular conformation predominates among the phenylcyclopropanes.[37–39] According to Ibers,[40] this preference is partly due to donation of electron density from the phenyl group to the cyclopropane $4e'$ orbital, but presumably steric interactions between R^2 and the bromo atom *cis* to CH_2R^2 are even more important. This is supported by AM1 calculations (*vide infra*).

Semiempirical calculations. In an attempt to gain information about restrictions related to rotation about the C2–C4 bond in the *gem*-dihalocyclopropanes under investigation, AM1 calculations were performed on 1,1-dibromo-2-ethyl-2-phenylcyclopropane (**16**), regarded as a representative model compound for cyclopropanes **1–13**, and 1-ethyl-1-phenylcyclopropane (**17**), a compound used to estimate the effect of the bromine atoms. The results from the grid mapping are shown as contour plots in Fig. 4, where α is used for the torsion of the phenyl ring relative to the ethyl substituent and β is the rotation of the ethyl group relative to the phenyl group. When α = β = 0° the ethyl group is eclipsed with the phenyl ring and the carbon atoms of the two groups constitute a planar system. From Fig. 4 it

Table 7. Energy minima and corresponding torsional angles θ_1 and θ_2, as defined by Bystrov and Stepanyants,[33] of 1-ethyl-1-phenylcyclopropane (**17**) and 1,1-dibromo-2-ethyl-2-phenylcyclopropane (**16**) as identified by torsional forcing of β and rotation of α (all angles in °).

Conformation[a]	α	β[b]	Energy/kcal mol^{-1}	θ_1[c]	θ_2(H41)[c]	θ_2(H42)[c]
17-I	80.1	73.1	34.67	143.6	47.7	164.6
16-I	97.5	64.7	49.97	142.6	45.0	160.9
17-II	98.1	164.9	35.41	142.5	141.3	−103.0
17-III	79.9	−163.8	35.41	140.3	174.1	−70.2
16-III	111.0	−132.0	50.57	144.2	−158.6	−43.0
17-IV	98.0	−72.8	34.67	143.0	−96.4	20.5
16-IV	109.6	−67.3	49.59	144.0	−92.0	25.5

[a]Consult Fig. 5 for notations. [b]In order to emphasize the symmetry in **17** the rotation of β is taken from −180 to 180°. [c]Consult Fig. 2 for notations.

is evident that compound **17** possesses two energy minima which both correspond to a *gauche* conformation; the position of the phenyl group is somewhat different for the two conformers.

The minima of **16** and **17** were further investigated by performing a torsional forcing of the ethyl group (β) and concomitantly a free rotation of the phenyl group (α). The results of these computations are shown in Fig. 5. From the lower curve it is apparent that **17** exhibits two local minima, II and III, close to β = 180° because of interaction between the phenyl group and the *cis*-hydrogen atoms attached to the cyclopropane ring. When two geminal hydrogens are replaced by a *gem*-dibromo moiety, however, significant steric interactions develop between the phenyl group and the *cis*-bromo atom, and one of the local minima, III, of **17** is reduced almost to a plateau, whereas the other, II, disappears owing to development of a significant energy barrier, which is larger than 6 kcal mol^{-1} for **16** as compared to less than 2 kcal mol^{-1} for **17**.

A full optimization over all degrees of freedom has been carried out for all minima indicated in Fig. 5. The results, which are summarized in Table 7, clearly show that the energy differences between the various conformations are rather small. For conformation IV, which is the global minimum for both **16** and **17**, the effect of bromine substitution is rather small. The main difference is found in conformers II and III, where the interaction between the bromine atom and the ethyl group is the largest. For conformation I the effect is quite small for β, but somewhat larger for α.

A plot of the most stable conformation of dibromide **16** (IV), as borne out by AM1 calculations, is shown in Fig. 6, and in Table 7 the corresponding torsional angles θ_1 and θ_2, as defined by Bystrov and Stepanyants (Fig. 2), are included. It is noteworthy that this conformation is very close to the solid-state conformations of **1**,[9] as well as of **5**, **6** and **8** (Fig. 1 and Table 3). Furthermore, by addition of less than 3 kcal mol^{-1} (Fig. 5), **16** can rotate approximately 120° counterclockwise and attain conformation I (Fig. 5), which is very close to the solid-state conformation of **13** (Fig. 1 and Table 3).

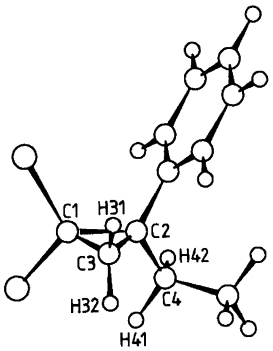

Fig. 6. Plot of the conformation of 1,1-dibromo-2-ethyl-2-phenylcyclopropane (**16**) that is most stable according to AM1 calculations.

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