Carbon-13 Nuclear Magnetic Resonance Spectroscopy of 1-Aryl-2,2-dibromocyclopropanes

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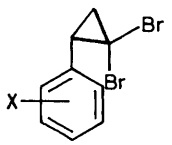
The ^{13}C NMR spectra of 12 1-aryl-2,2-dibromocyclopropanes have been measured and 1-phenyl-2,2-dibromocyclopropanes was studied under different conditions of concentration, solvent, and temperature. The results suggest that the field effect is mainly responsible for the substituent chemical shift (SCS) for C-β. The ^{13}C shifts for carbons on both the cyclopropyl and the phenyl rings are dependent upon concentration and solvent.

In the past, quite a few chemists have studied cyclopropanes because of their unique properties and uses.[1] Pews and Ojha[2] reported ^{18}F NMR shielding parameters for a series of *p*-fluoro-*m'*- and -*p'*-substituted 1,2-diphenylethanes, 1,2-diphenylethylenes, and 1,2-diphenylcyclopropanes thus providing quantitative information regarding the ability of the cyclopropane ring to transmit the conjugation effect. The ^{13}C n.m.r. studies were also carried out for cyclopropylbenzene and the 1-aryl-2,2-dichlorocyclopropanes.[3-4] These studies demonstrate that the substituent effect on the C-α and C-β is different for each. The hyperconjugative resonance effect was attributed to the former.[3] Subsequently, the authors emphasized the reverse substituent effect and ^{13}C NMR conformational dependency and gave no correlation between the SCS and the Hammett substituent constant (σ).[4]

The ^{13}C chemical shift is well correlated with the electron density of carbon derived from CNDO/2 calculations.[5] Therefore, the SCS of carbon would represent the variation of electron densities upon changing the substituent. The SCS dependence on substituents can be treated with the dual substituent parameter (DSP) method, which mainly includes both the inductive effect and the resonance effect proposed by Swain and Lupton.[8]



(1)

X=H, *m*-Br, *p*-Br, *m*-Cl, *p*-Cl, *m*-CH_3, *p*-CH_3, *p*-$(CH_3)_2N$, *p*-F, *p*-NO_2, *m*-OCH_3, *p*-OCH_3.

In this work, we report the ^{13}C NMR dependence upon the substituents, temperature, solvent, and concentration, and analyse further the weighting factors of field (*f*), and resonance (*r*) of the substituent on 1-aryl-2,2-dibromocyclopropanes.

Experimental

^{13}C NMR measurements.—The NMR data of 10 vol% of analyte in $CDCl_3$ (unless specified solvents or concentration) were recorded on a Bruker AC-250 spectrometer at 62.9 MHz; 64K data points were collected within a range of 10 kHz. All chemical shifts were measured relative to $SiMe_4$ in proton noise decoupled spectra. Assignments were assisted by the proton coupled spectra.

Chemicals.—*p*-Bromo-, *m*-bromo-, *p*-chloro-, *m*-chloro-, *p*-fluoro-, and *m*-methyl-styrenes were obtained from commercial sources. *p*-Methoxy-, *m*-methoxy-, *p*-methyl-, and *p*-dimethylaminostyrenes were prepared from the corresponding benzaldehydes by means of the Wittig reaction.[7] 1-Aryl-2,2-dibromocyclopropanes were prepared by treating styrene with $CHBr_3$ in pentane in the presence of $KOBu^t$ in accordance with the literature procedures.[8] 1-(*p*-Nitrophenyl)-2,2-dibromopropane was prepared directly from nitration of phenylcyclopropane.[9]

The analytical data and physical properties of new dibromocyclopropanes are summarized as following:

1-(p-*Bromophenyl*)-2,2-*dibromocyclopropane*. M.p. 63–64 °C; δ_H 1.87–2.23 (2 H, m), 2.89 (1 H, t, *J* 9.5 Hz), 7.07–7.54 (4 H, m); Calc. for $C_9H_7Br_3$: C, 30.5; H, 2.0. (Found: C, 30.5; H, 2.0).

1-(p-*Chlorophenyl*)-2,2-*dibromocyclopropane*. M.p. 51–52 °C. δ_H 1.87–2.23 (2 H, m), 2.91 (1 H, t, *J* 7.5 Hz), 7.12–7.35 (4 H, m); Calc. for $C_9H_7Br_2Cl$, C, 34.8; H, 2.3%. (Found: C, 34.8; H, 2.0).

1-(m-*Chlorophenyl*)-2,2-*dibromocyclopropane*. B.p. 105–110 °C/0.8 Torr;† δ_H 2.01 (1 H, d, *J* 8.6 Hz), 2.07 (1 H, d, *J* 9.0 Hz), 2.91 (1 H, t, *J* 9.0 Hz), 7.06–7.30 (4 H, m); Calc. for $C_8H_7Br_2Cl$: C, 34.8, H, 2.3%. (Found: C, 34.8; H, 2.35).

1-(p-*Fluorophenyl*)-2,2-*dibromocyclopropane*. B.p. 87 °C/1.5 Torr; δ_H 1.85–2.21 (2 H, m), 2.85 (1 H, dd, J_{ac} 8.6, J_{bc} 10.3 Hz), 6.93–7.28 (4 H, m); Calc. for $C_9H_7Br_2F$: C, 36.8, H, 2.4%. (Found: C, 36.9, H, 2.5).

1-(p-*Methoxyphenyl*)-2,2-*dibromocyclopropane*. B.p. 106–108 °C/1.5 Torr; δ_H 2.0–2.34 (2 H, m), 3.05 (1 H, t, *J* 9.5 Hz), 3.96 (3 H, s), 6.6–7.1 (4 H, m); Calc. for $C_{10}H_{10}Br_2O$: C, 39.2; H, 3.3%. (Found: C, 39.25, H, 3.3).

1-(m-*Methoxyphenyl*)-2,2-*dibromocyclopropane*. B.p. 143 °C/6 Torr; δ_H 1.89–2.21 (2 H, m), 2.93 (1 H, dd, J_{ac} 8.6, J_{bc} 10.3 Hz), 3.81 (3 H, s), 6.79–7.34 (4 H, m); Calc. for $C_{10}H_{10}Br_2O$: C, 39.2, H, 3.3%; (Found: C, 39.3, H, 3.25).

1-(p-*Tolyl*)-2,2-*dibromocyclopropane*. B.p. 95–96 °C/0.9 Torr; δ_H 1.83–2.22 (2 H, m), 2.35 (3 H, s), 2.93 (1 H, t, *J* 8.4 Hz), 7.15–7.27 (4 H, m); Calc. for $C_{10}H_{10}Br_2$: C, 41.4; H, 3.5%. (Found: C, 41.4; H, 3.4).

1-(m-*Tolyl*)-2,2-*dibromocyclopropane*. B.p. 115 °C/10 Torr; δ_H 1.93–2.23 (2 H, m), 2.41 (3 H, s), 2.96 (1 H, dd, J_{ac} 8.6, J_{bc} 10.3 Hz), 7.02–7.36 (4 H, m); Calc. for $C_{10}H_{10}Br_2$: C, 41.4, H, 3.5%. (Found: C, 41.4, H, 3.5).

1-(p-*Dimethylaminophenyl*)-2,2-*dibromocyclopropane*. M.p. 50–53 °C; δ_H 1.83–2.00 (2 H, m), 2.82 (1 H, m), 2.85 (6 H, s), 6.61 (2 H, dd, *J* 6.8 and 2.0 Hz) 7.02 (2 H, dd, *J* 6.8 and 2.0 Hz); Calc. for $C_{11}H_{13}Br_2N$: C, 41.3; H, 4.4% (Found: C, 41.2; H, 4.4).

† 1 Torr = 133.322 Pa.

Table 1. ^{13}C Chemical shifts for 1-aryl-2,2-dibromocyclopropanes in deuteriochloroform (ppm from TMS as internal standard).

R	C-α	C-β	C-γ	C-1	C-2	C-3	C-4	C-5	C-6	others
p-NO_2	36.67	26.22	29.01	144.11	130.67	124.34	147.01	124.34	130.55	
m-Br	36.70	27.28	28.79	138.35	133.08	123.08	131.85	131.03	128.75	
m-Cl	36.03	27.22	28.01	138.34	129.43	134.59	128.20	129.95	127.61	
p-Br	36.03	27.70	28.08	135.46	131.01	131.89	122.10	131.89	131.01	
p-Cl	35.45	27.68	28.68	134.40	131.22	129.46	134.42	129.38	131.12	
m-OCH_3	37.66	28.02	29.11	138.97	116.32	160.95	114.54	130.79	122.78	57.04
p-F	35.88	28.15	28.20	132.20	131.10[a]	115.77[b]	162.57[c]	115.77[b]	131.01[a]	
H	36.88	28.42	27.18	135.93	128.25	127.57	128.86	127.57	128.25	
m-CH_3	35.86	28.65	27.13	135.59	129.49	137.63	128.14	127.91	126.56	21.45
p-CH_3	35.62	28.95	27.19	132.77	128.56	128.78	137.05	128.78	128.56	21.26
p-OCH_3	35.45	29.24	27.48	128.10	129.78	113.61	158.58	113.61	129.78	55.25
p-$(CH_3)_2N$	35.30	30.41	27.06	123.63	129.49	111.94	149.74	111.94	129.49	40.40

Doublet centre corresponding to [a] J_{CF} 8; [b] J_{CF} 22; [c] J_{CF} 245.6 Hz.

Table 2. SCS (in ppm) of 1-aryl-2,2-dibromocyclopropanes in deuteriochloroform solution (positive values represent downfield shifts).

R	σ	C-α	C-β	C-γ
p-NO_2	+0.78	−0.21	−2.20	+1.83
m-Br	+0.39	−0.18	−1.14	+1.61
m-Cl	+0.37	−0.85	−1.20	+0.83
p-Br	+0.23	−0.85	−0.72	+0.90
p-Cl	+0.23	−1.43	−0.72	+1.50
m-OCH_3	+0.12	+0.78	−0.40	+1.93
p-F	+0.06	−1.00	−0.27	+1.02
H	0.00	(36.88)	(28.42)	(27.18)
m-CH_3	−0.17	−1.02	+0.23	−0.05
p-CH_3	−0.17	−1.26	+0.53	+0.01
p-OCH_3	−0.27	−0.43	+0.82	+0.30
p-$(CH_3)_2N$	−0.83	−1.58	+1.98	−0.12

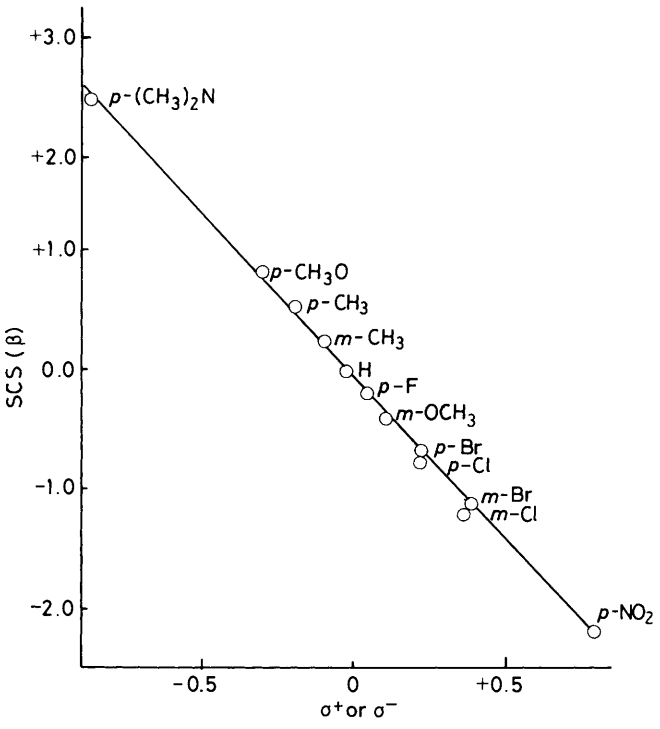


Figure 1. Carbon-13 SCS(β) values in ppm for 1-aryl-2,2-dibromocyclopropanes *vs.* Hammett substituent constants (σ).

Results and Discussion

Substituent Effect.—The ^{13}C chemical shifts of 12 1-aryl-2,2-dibromocyclopropanes are summarized in Table 1. The chemical shifts of C-α and C-γ of the above compounds are further downfield than those of 1-arylcyclopropanes and 1-aryl-2,2-dichlorocyclopropanes. The C-β shifts are further upfield than those of dichloro-analogues due to the heavy atom factor.[10] The SCS (α,γ) values are changed irregularly. However, in general SCS(β) values are shifted upfield when the substituents on the aromatic rings are electron-donating groups, and *vice versa.* (Table 2) This phenomenon correlates well with Hammett substituent constants (σ). (Figure 1) There appears to be an inflection in the correlation line which corresponds to a slope of −2.75 (r = 0.985) for the groups varying from *p*-dimethylamino (σ = −0.83) to *p*-NO_2 (σ = +0.78) in contrast with those of arylcyclopropanes (positive slope with no common correlation line between electron-donating and electron-attracting substituents) (see Table 2). The ^{13}C NMR provides information which shows that the interaction of the substituent on C-β through the phenyl ring is different for the aryl- and the 1-aryl-2,2-dibromocyclopropane system. The effect on C-β through phenyl rings should be accentuated by the inductive, and the resonance effect as well as by a significant conformational effect.[11]

The DSP treatment has been extensively applied to the substituent effects on the aromatic system.[5] Information on the relative contribution of inductive and resonance effects can be obtained by correlation of the SCS with the field, F, and the resonance, R, substituent constants of Swain and Lupton.[6] The results of correlations carried out for the title compounds, together with values reported for cyclopropanes and isopropylbenzenes are listed in Table 3.[3] The correlations for this series are divided into *para-* and *meta*-substituents because of the different nature of these positions. The coefficients determined for the *para*-substituted 1-aryl-2,2-dibromocyclopropanes are the best among the three sets of compounds. The weighting factors, field effect, f, and resonance, r, of C-β in both the *meta-*, and the *para*-substituted compounds is quite different from those of isopropylbenzenes and cyclopropylbenzenes. The contribution of the field effects to the resonance is 74 ± 7, 90 ± 3 for *meta-* and *para*-substituted compounds, respectively. The field effect mainly contributes to the SCS of C-β, which is not in agreement with that of other series of compounds. This is the main reason for the negative slope (as opposed to positive for other systems) obtained for the correlation of the SCS.[3]

Concentration Effect.—The halogenated solvents display the deshielding phenomenon which increases with increasing number of halogens (except for fluorine) per molecule.[12]

Table 3. Correlation between SCS of C-β and the Swain–Lupton substituent constants F and R.

Compounds	chemical shift	f^a	r	field (%)	correlation coefficient
1-aryl-2,2,-dibromocyclopropanes	C-β(*para*-)	1.758 ± 0.054	0.198 ± 0.064	90 ± 3	0.986
	C-β(*meta*-)	−1.709 ± 0.161	0.601 ± 0.132	74 ± 7	0.921
cyclopropylbenzene[b]	C-α	0.130 ± 0.150	1.483 ± 0.189	10 ± 10	0.961
	C-β	0.962 ± 0.268	2.248 ± 0.337	35 ± 7	0.966
isopropylbenzene[b]	C-α	0.004 ± 0.114	1.319 ± 0.145	—	0.975
	C-β	−0.318 ± 0.068	−0.578 ± 0.087	41 ± 6	0.979

[a] f and r are weighting factors in the equation $\delta = fF + rR + \delta_0$. [b] Ref. 3.

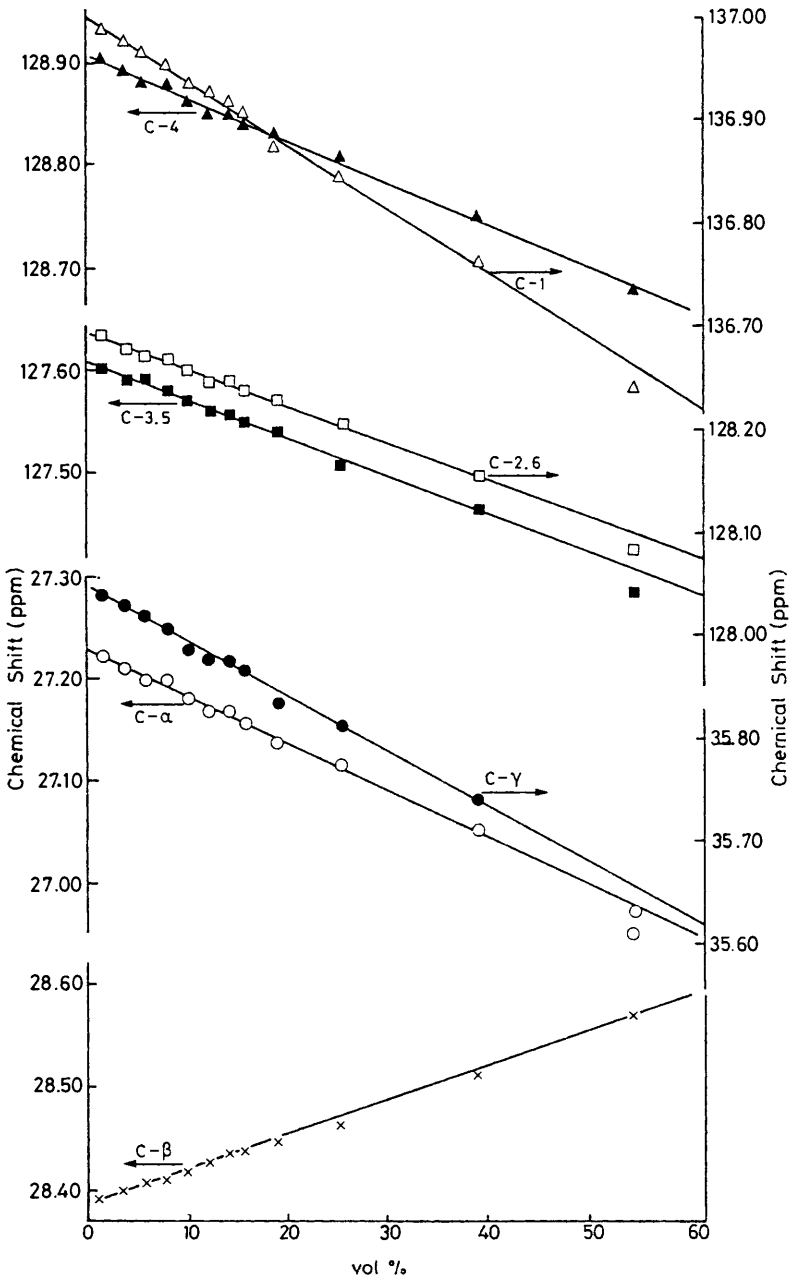


Figure 2. Concentration dependence of the ^{13}C chemical shifts of 1-phenyl-2,2-dibromocyclopropane in deuteriochloroform.

Therefore, the chemical shifts of the analyte should vary with changes in the concentrations in $CDCl_3$ (*i.e.* changing the mole ratio of the solvent to analyte). In this work, the concentration of 1-phenyl-2,2-dibromocyclopropane (**1**:X=H) is varied from 1.4–53 vol% in $CDCl_3$ (Table 4). The chemical shifts decrease linearly on increasing the concentration. This fact agrees well

Table 4. ^{13}C Chemical shifts (in ppm) for 1-phenyl-2,2-dibromocyclopropane in deuteriochloroform at various concentrations.

vol%	C-α	C-β	C-γ	C-1	C-2,6	C-3,5	C-4
1.4	27.22	28.39	35.93	135.98	128.28	127.60	128.90
3.7	27.21	28.40	35.92	135.97	128.27	127.59	128.89
5.9	27.20	28.41	35.91	135.96	128.26	127.59	128.88
8.0	27.20	28.41	35.90	135.95	128.26	127.58	128.88
10.0	27.18	28.42	35.88	135.93	128.25	127.57	128.86
12.0	27.17	28.43	35.87	135.92	128.24	127.56	128.85
14.0	27.17	28.44	35.87	135.91	128.24	127.56	128.85
15.5	27.16	28.44	35.86	135.90	128.23	127.55	128.84
18.7	27.14	28.45	35.83	135.87	128.22	127.54	128.83
24.0	27.12	28.46	35.81	135.84	128.20	127.52	128.81
38.2	27.06	28.51	35.74	135.76	128.15	127.47	128.75
53.1	26.96	28.58	35.63	135.63	128.08	127.39	128.68

Table 5. ^{13}C Chemical shifts (in ppm) for phenylcyclopropane in deuteriochloroform at various concentrations.

vol%	C-α	C-β	C-1	C-2,6	C-3,5	C-4
5.0	15.35	9.15	143.95	125.63	128.23	125.32
10.0	15.34	9.14	143.92	125.62	128.22	125.31
15.0	15.33	9.14	143.88	125.60	128.20	125.29
20.0	15.32	9.12	143.86	125.58	128.18	125.28
30.0	15.31	9.08	143.79	125.55	128.15	125.25
40.0	15.30	9.06	143.74	125.52	128.12	125.22
60.0	15.28	9.01	143.67	125.47	128.06	125.17

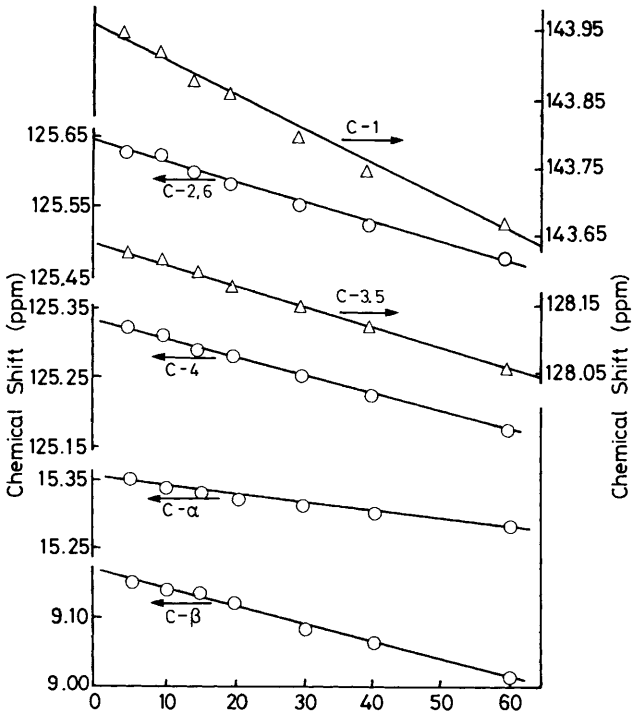


Figure 3. Concentration dependence of the ^{13}C chemical shifts of phenylcyclopropane in deuteriochloroform.

with the prediction except for the C-β atom as shown in Table 3 and Figure 2. This contradictory behaviour of C-β compared with other carbon atoms in the same environment indicates that the additional interaction within the compound itself must be considered. This is consistent with the DSP treatment, while also demonstrating that the field effect is an important factor.

From Table 5 and Figure 3, we can discover that the concentration dependence of chemical shifts of C-α, C-1, C-2,6, C-3,5, and C-4 of phenylcyclopropane (**2**) is same as that of compound (**1**). However, the concentration effect on the C-β of compound (**1**) is just the opposite of that of compound (**2**). This result suggests that the interactions between the phenyl ring and C-β of cyclopropanes are different and confirms the results from DSP treatment.

Temperature Effect.—The chemical shift of alkyl or cyclopropyl groups attached to the phenyl ring has been shown to be dependent on conformation.[4] Increasing temperature of the solution should increase vibrations of the molecules and possibly change the conformation of the analyte. If that is true, then the chemical shifts of the analyte should be altered by different temperature conditions. The investigation of the temperature effect on the chemical shifts was carried out using compound (**1**) (25 vol%) in $(CD_3)_2SO$ solution because of the stability of this solvent even at relative high temperatures. On raising the temperature from 300 to 400 K, the chemical shift only varies as much as 0.02 ppm, this small number is within instrumental error. Therefore, the temperature effect seems not to be significant.

Solvent effect.—For the interaction field of a polar molecule in a medium of relative permittivity, ε_r, the ^{13}C screening constants in substituted methanes should depend linearly on the function, $(\varepsilon_r - 1)/(2 + 2n)$, where n is the refractive index of the solvent molecules.[13] Also, the difference between the methane shift in a given solvent is found in the linear relationship with ΔH_r. This indicates that the van der Waals interaction between analyte and solvent plays an important role.[10] However, the predication based on both proposals fails to account for the solvent dependence of ^{13}C chemical shift for this series of compounds.

We conclude from this work that the chemical shifts are mainly affected by two factors, *i.e.* the shielding ability and relative permittivity of solvents. The latter can be more important to a polarized bond because that solvent with higher relative permittivity should be able to stabilize the polarized bond better and result in redistribution of the electron density of that bond. The electron distribution from CNDO/2 calculation is well correlated with ^{13}C chemical shifts.[5] The ^{13}C chemical shifts of compound (**1**) in various solvents are given in Table 6. Some chemical shifts are obscured by the solvents (*i.e.* $[^2H_6]$-acetone, C_6D_6, and C_6D_{12}). The difference in chemical shifts in various solvents is obtained by comparison with those in $CDCl_3$. The chemical shift depends very much upon the nature of solvent. In general, the C-β shifts to downfield in non-polar solvents and to upfield in polar solvents. The dish-shaped molecules (C_6D_6, $[^2H_5]$pyridine, and $[^2H_3]$nitromethane) would deshield the whole molecule of analyte.[13] The rod-like molecule ($[^3H_2]$acetonitrile) displays another kind of character.[10] Aprotic solvents ($[CD_3]_2SO$, $[^2H_6]$acetone) enhance the polarizability of C-β–Br bond and result in a downfield shift for C-β. The others are shielded by solvents. On the other hand, the protic solvent (CD_3OD) forms hydrogen bonds[14] with the phenyl ring leading to another kind of pattern. The difference in solvent-induced shift for C-β is 2.6 ppm for cyclohexane and nitromethane. This value is much less than that of ethyl iodide, for which the solvent-induced shift is 5.2 ppm.[15]

In general, the chemical shifts of compound (**2**) are less solvent dependent (Table 7). Although, the combination of shielding effect, dielectric effects, and the nature of solvents as well as analytes complicate the results from the solvent effect. However, the polarizability of polar bonds in higher relative permittivity medium still plays an important role. Compound (**2**) contains less polar bonds than compounds (**1**) do, and results in less variation in chemical shift from various solvents.

Table 6. Solvent dependence of the ^{13}C chemical shifts (in ppm) of 1-phenyl-2,2-dibromocyclopropane.[a]

Solvent	C-α	C-β	C-γ	C-1	C-2,6	C-3,5	C-4
CD_3COCD_3	26.05 (−1.15)	—[b]	35.14 (−0.77)	135.45 (−0.51)	127.68 (−0.59)	126.95 (−0.64)	128.38 (−0.50)
CD_3CN	27.45 (+0.25)	29.76 (+1.35)	36.46 (+0.55)	137.12 (+1.16)	129.20 (+0.93)	128.49 (+0.90)	129.83 (+0.95)
C_6D_6	27.46 (+0.26)	29.36 (+0.95)	36.56 (+0.65)	136.55 (+0.59)	—[b]	—[b]	129.61 (+0.73)
$CDCl_3$	27.20	28.41	35.91	135.96	128.27	127.59	128.88
C_6D_{12}	—[b]	27.51 (−0.90)	36.61 (+0.70)	136.40 (0.44)	128.65 (+0.38)	127.69 (+0.10)	129.14 (+0.26)
CD_3SOCD_3	26.06 (−1.14)	29.63 (+1.22)	34.80 (−1.11)	135.81 (−0.15)	128.13 (−0.14)	127.35 (−0.24)	128.69 (−0.19)
CD_3OD	27.72 (+0.52)	29.42 (+1.01)	37.61 (+1.70)	137.49 (+1.53)	129.26 (+0.99)	128.52 (+0.93)	129.97 (+1.09)
CD_3NO_2	27.76 (+0.56)	30.13 (+1.72)	36.89 (+0.98)	137.70 (+1.74)	129.60 (+1.33)	128.88 (+1.29)	130.22 (+1.34)
C_5D_5N	27.07 (−0.13)	29.69 (+1.28)	36.06 (+0.15)	136.54 (+0.58)	128.64 (+0.37)	127.87 (+0.28)	129.33 (+0.45)

[a] The relative chemical shifts compared with the values in deuteriochloroform are shown in parentheses. [b] Chemical shifts not assigned due to complexity of the spectrum.

Table 7. Solvent dependence of the ^{13}C chemical shifts (in ppm) of phenylcyclopropane.[a]

Solvent	C-α	C-β	C-1	C-2,6	C-3,5	C-4
CD_3COCD_3	14.97 (−0.37)	8.71 (−0.43)	143.90 (−0.02)	125.39 (−0.23)	128.12 (−0.10)	125.17 (−0.14)
CD_3CN	14.33 (−1.01)	9.21 (+0.07)	144.49 (+0.57)	125.81 (+0.19)	128.67 (+0.45)	125.69 (+0.38)
C_6D_6	16.18 (+0.84)	9.73 (+0.59)	144.52 (+0.60)	126.48 (+0.86)	129.09 (+0.87)	126.11 (+0.80)
$CDCl_3$	15.34	9.14	143.92	125.62	128.22	125.31
C_6D_{12}	16.51 (+1.17)	9.62 (+0.48)	144.65 (+0.73)	127.65 (+2.03)	129.96 (+1.76)	127.22 (+1.91)
CD_3SOCD_3	14.98 (−0.36)	9.23 (+0.09)	143.58 (−0.34)	125.25 (−0.37)	128.12 (−0.10)	125.14 (−0.37)
CD_3OD	16.07 (+0.73)	9.33 (+0.19)	145.15 (+1.23)	126.50 (+0.92)	129.15 (+0.93)	126.24 (+0.93)
CD_3NO_2	16.25 (+0.91)	10.05 (+0.91)	145.65 (+1.70)	126.78 (+1.16)	128.68 (+0.34)	126.67 (+1.36)
C_5D_5N	15.74 (+0.40)	9.59 (+0.45)	144.32 (+0.40)	126.01 (+0.39)	128.68 (+0.46)	125.74 (+0.44)

[a] The relative chemical shifts compared with the values in deuteriochloroform are shown in parentheses.

Conclusions

The ^{13}C NMR resonances of 1-aryl-2,2-dibromocyclopropanes are strongly dependent not only on the nature of substituents but on the nature of solvents and the concentration of analyte. The inverse substituent dependence is due to the field effect (90 ± 3 for *para*-substituted and 74 ± 7 for *meta*-substituted) rather than the hyperconjugative effect. Changes due to the solvent effect include hydrogen bonding (CD_3OD), deshielding ([$^2H_1$]chloroform, C_6D_6, [$^2H_5$]pyridine, and [$^2H_3$]nitromethane), and shielding [$^2H_3$]acetonitrile) as well as the polar–polar interaction in aprotic solvents {$(CD_3)_2SO$, [$^2H_6$]-acetone}. Also, changes due to concentration effect in $CDCl_3$ further demonstrate its deshielding character.

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