Molecular Polarisability. A Conformational Study of Some Substituted Arylcyclopropanes

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The dipole moments and molar Kerr constants of the following substituted cyclopropanes have been measured in cyclohexane solution: 1,1-dichloro-2-p-chlorophenyl-2-methylcyclopropane, 1,1-dichloro-2-p-tolylcyclopropane, 1,1-dichloro-2-mesitylcyclopropane, 1,1-dichloro-2,2-diphenylcyclopropane, 1,1-dichloro-2,2-dimethyl-3-phenylcyclopropane, 1,1-dichloro-2,2,3,3-tetramethylcyclopropane, hexabromocyclopropane, 1,1-dibromo-2-phenylcyclopropane, 1,1-dibromo-2-p-tolylcyclopropane, 1,1-dibromo-2-p-bromophenylcyclopropane, and 1,1-dibromo-2,2-diphenylcyclopropane. The data are analysed to deduce the preferred solution state conformations.

IN arylcyclopropanes the conjugative interaction between the C_3 nuclear electrons and the π electron system of the aromatic substituent group is maximal for conformations in which the aromatic and cyclopropyl group planes are mutually orthogonal.[1-4] The resonance stabilisation of geometric forms of this type has been experimentally verified in the case of phenylcyclopropane.[4] It was shown by Le Fevre et al.,[5] however, that insertion of a vicinal (cis) chloro-substituent in phenylcyclopropane causes a steric deflection of the phenyl group away from the preferred ' orthogonal ' disposition. In this work we explore further the competitive steric and mesomeric influences in a variety of substituted phenylcyclopropanes.

EXPERIMENTAL

Materials, Apparatus, etc.—The solutes were prepared by standard procedures [6,7] and were purified immediately before use to give: 1,1-dichloro-2-p-chlorophenyl-2-methylcyclopropane, b.p. 135—136° at *ca.* 8·5 mmHg; 1,1-dichloro-2-p-tolylcyclopropane, b.p. 138—139° at *ca.* 31 mmHg; 1,1-dichloro-2-mesitylcyclopropane, b.p. 89—91° at *ca.* 0·7 mmHg; 1,1-dichloro-2,2-diphenylcyclopropane, m.p. 110—112°; 1,1-dichloro-2,2-dimethyl-3-phenylcyclopropane, b.p. 111—112° at *ca.* 7 mmHg; 1,1-dichloro-

2,2,3,3-tetramethylcyclopropane, m.p. 51·5—52°; hexabromocyclopropane, m.p. 193—195°; 1,1-dibromo-2-phenylcyclopropane, b.p. 86—87° at *ca.* 1 mmHg; 1,1-dibromo-2-p-tolylcyclopropane, b.p. 151—153° at *ca.* 29 mmHg; 1,1-dibromo-2-p-bromophenylcyclopropane, m.p. 69—71°; and 1,1-dibromo-2,2-diphenylcyclopropane, m.p. 151—152°. Cyclohexane, as solvent, was dried over sodium, distilled, and then stored with sodium. The following constants apply for the solvent at 25°: $\varepsilon_1 = 2{\cdot}0199$, $d_1 = 0{\cdot}77389$, $(n_1)_D = 1{\cdot}4235$, $10^7(B_1)_D = 0{\cdot}054$, $10^{14}(_sK_1) = 1{\cdot}35$. The apparatus, techniques, symbols used, and methods of calculation have been described before.[8-11] The experimental results are summarised in Table 1.

DISCUSSION

Conformations of the 2-Aryl-1,1-*dichlorocyclopropanes.* —With each of the 2-aryl-1,1-dichlorocyclopropanes examined, theoretical molar Kerr constants were calculated for conformations defined by angles of rotation ϕ of the phenyl group from the reference ' orthogonal ' model shown in Figure 1 for which $\phi = 0°$. The sense of the rotation is *away* from the CCl_2 grouping as indicated by the arrow in Figure 1. The computational procedure is

[1] W. A. Bernett, *J. Chem. Educ.,* 1967, **44**, 17.

[2] G. L. Closs and H. B. Klinger, *J. Amer. Chem. Soc.,* 1965, **87**, 3265.

[3] J. P. Pete, *Bull. Soc. chim. France,* 1967, 357.

[4] L. V. Vilkov and N. I. Sadova, *Doklady Akad. Nauk. S.S.S.R.,* 1965, **162**, 565.

[5] R. S. Armstrong, M. J. Aroney, A. Hector, P. Hopkins, R. J. W. Le Fèvre, and W. Lüttke, *J. Chem. Soc. (B),* 1971, 1499.

[6] M. Makosza and M. Wawrzyniewicz, *Tetrahedron Letters,* 1969, **53**, 4659.

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[8] C. G. Le Fèvre and R. J. W. Le Fèvre, *Rev. Pure Appl. Chem.,* 1955, **5**, 261.

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[10] C. G. Le Fèvre and R. J. W. Le Fèvre, in ' Physical Methods of Organic Chemistry,' ed. A. Weissberger, Interscience, New York, 3rd edn., vol. 1, ch. XXXVI, p. 2459.

[11] R. J. W. Le Fèvre and G. L. D. Ritchie, *J. Chem. Soc.,* 1963, 4933.

summarised in ref. 12. For each conformational form studied the elements of the molecular polarisability tensor matrix b_{xx}, b_{yy}, etc., were calculated, with reference to the system of axes, X,Y,Z of Figure 1, from additivity of component group parameters. The following bond and group polarisability data * were used: b_1(cyclopropane) $= b_2$(cyclopropane) $= 6.00$, b_3(cyclopropane) $= 4.55$;[13] b_L(C–H) $= b_T$(C–H) $= b_V$(C–H) $= 0.65$;[14] b_L(C–Cl) $= 3.44$, b_T(C–Cl) $= b_V$(C–Cl) $= 2.05$;[5]

and each of the bonds C(cyclopropane)–Cl and C(cyclopropane)–Me was taken[19] in each case as 56° while the corresponding angle with the C(phenyl)–C(cyclopropyl) bond was assumed to be 51.5° (from ref. 4). Trial calculations were made to show that small variations ($\pm 2°$) in these angles do not significantly affect the conclusions. A test application of the group polarisability data was made in calculating the molar Kerr constant of phenylcyclopropane using an electric moment

TABLE 1

Molar polarisations and refractions, dipole moments, and molar Kerr constants (from observations on cyclohexane solutions at 25°)

Solute	Concentration range $10^5 w_2$	$\alpha\varepsilon_1$ *	β *	γ *	δ *	∞P_2 (cm³)	R_D (cm³)	μ(D) †	$10^{12} \infty(_m K_2)$ ‡
1,1-Dichloro-2-p-chlorophenyl-2-methylcyclopropane	611—3074	2.00	0.394	0.051	−21.8	160	58.9	2.19	−70.7
1,1-Dichloro-2-p-tolylcyclopropane	579—4829	2.20	0.340	0.053	6.35	150	54.0	2.13	15.9
1,1-Dichloro-2-mesitylcyclopropane	388—2911	1.83	0.320	0.056	8.49	152	63.8	2.04	25.4
1,1-Dichloro-2,2-diphenylcyclopropane	1295—4531	1.60	0.371	0.075	−18.9	155	73.8	1.95	−67.9
1,1-Dichloro-2,2-dimethyl-3-phenylcyclopropane	1197—4139	2.19	0.326	0.053	31.0	161	58.9	2.20	88.6
1,1-Dichloro-2,2,3,3-tetramethylcyclopropane	319—2189	3.15	0.279	0.022	20.2	166	43.3	2.43	43.6
Hexabromocyclopropane	411—1437	0.23	0.786	0.049	2.43	64.7	61.2	0	17.2
1,1-Dibromo-2-phenylcyclopropane	506—7029	1.36	0.566	0.054	0	130	54.0	1.89	−1.1
1,1-Dibromo-2-p-tolylcyclopropane	1148—4696	1.51	0.534	0.055	20.7	150	59.9	2.06	79.5
1,1-Dibromo-2-p-bromophenylcyclopropane	914—3467	1.11	0.629	0.055	−17.2	138	62.4	1.88	−83.8
1,1-Dibromo-2,2-diphenylcyclopropane	770—1420	1.15	0.514	0.069	−9.37	153	79.9	1.84	−45.3

* Incremental changes in the dielectric constants, densities, refractive indices, and Kerr constants ($\Delta\varepsilon$, Δd, Δn, and ΔB, respectively) were measured for solutions having solute weight fractions w_2. The coefficients, $\alpha\varepsilon_1$, β, γ, and δ, were derived from the relations: $\alpha\varepsilon_1 = \Sigma\Delta\varepsilon/\Sigma w_2$; $\beta = \Sigma\Delta d/d_1\Sigma w_2$; $\gamma = \Sigma\Delta n/n_1\Sigma w_2$; $\delta = \Sigma\Delta B/B_1\Sigma w_2$. † Calculated on the basis that $_D P = 1.05 R_D$. ‡ The term $_\infty(_m K_2)$ refers to the solute molar Kerr constant at infinite dilution.

b_L(C_6H_5–C) $= 11.9_5$, b_T(C_6H_5–C) $= 10.5_5$, b_V(C_6H_5–C) $= 7.15$;[15] b_L(C–C) $= 0.97$, b_T(C–C) $= b_V$(C–C) $= 0.26$;[14]
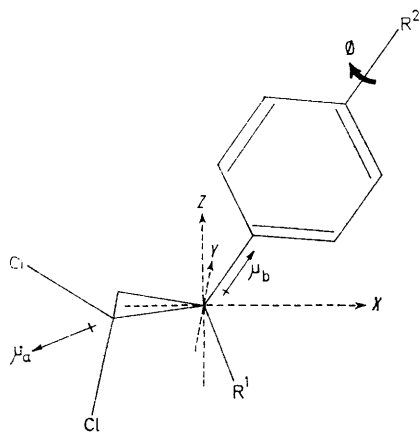
FIGURE 1 Orthogonal model for conformations of substituted phenylcyclopropanes

b_L(C_{ar}–CH_3) $= 3.4$, b_T(C_{ar}–CH_3) $= 2.0$, b_V(C_{ar}–CH_3) $= 2.3$;[16] b_L(C_{ar}–Cl) $= 4.3$, b_T(C_{ar}–Cl) $= 2.0_5$, b_V(C_{ar}–Cl) $= 1.5$;[17] b_L(mesityl) $= b_T$(mesityl) $= 16.4_9$, b_V(mesityl) $= 11.6_8$.[18] The angle between the cyclopropane ring plane

* The polarisability semi-axes of molecules b_1, b_2, or b_3, or of bonds and groups b_L, b_T, or b_V are quoted in Å³ units.

[12] R. J. W. Le Fèvre, Adv. Phys. Org. Chem., 1965, 3, 1.
[13] M. J. Aroney, R. J. W. Le Fèvre, W. Lüttke, G. L. D. Ritchie, and P. J. Stiles, Austral. J. Chem., 1968, 21, 2551.
[14] R. J. W. Le Fèvre, B. J. Orr, and G. L. D. Ritchie, J. Chem. Soc. (B), 1966, 273.

of 0.46 D (from dielectric loss measurements[20]) directed along the C(cyclopropyl)–C(phenyl) bond axis. The $_m K$(calc.) thus derived for this molecule has a spread of only four units, (21—25) $\times$ 10⁻¹², so that it is not possible to differentiate between the various allowable conformations; the experimental $_\infty(_m K_2)$ is $26 (\pm 2) \times 10^{-12}$. The direction of action of the measured molecular dipole moment was taken along the bisector axis of the Cl–C–Cl grouping except in the case of 1,1-dichloro-2-p-chlorophenyl-2-methylcyclopropane and 1,1-dichloro-2-p-tolylcyclopropane. For each of these two molecules the location was calculated on the basis that μ(resultant) is the vector sum of the components μ_a and μ_b (as shown in Figure 1) where μ_a equals, in turn, 1.91 D[5] (the moment of 1,1-dichloro-2-phenylcyclopropane) and 2.05 D[5] (the moment of 1,1-dichloro-2-methyl-2-phenylcyclopropane). The vector components μ_b thus derived are respectively 1.64 and −0.52 D. The former is 0.43 D lower than the moment reported by Nishida et al.[21] for p-chlorophenylcyclopropane and this we attribute to an inductive withdrawal of electrons from the phenylcyclopropane

[15] M. J. Aroney, K. E. Calderbank, R. J. W. Le Fèvre, and R. K. Pierens, J. Chem. Soc. (B), 1969, 159.
[16] R. J. W. Le Fèvre and L. Radom, J. Chem. Soc. (B), 1967, 1295.
[17] R. J. W. Le Fèvre and B. P. Rao, J. Chem. Soc., 1958, 1465.
[18] P. H. Gore, J. A. Hoskins, R. J. W. Le Fèvre, L. Radom, and G. L. D. Ritchie, J. Chem. Soc. (B), 1969, 485.
[19] J. M. O'Gorman and V. Schomaker, J. Amer. Chem. Soc., 1946, 68, 1138.
[20] M. J. Aroney, S. Filipczuk, and H. J. Stootman, unpublished data.
[21] S. Nishida, I. Moritani, and T. Sato, J. Amer. Chem. Soc., 1967, 89, 6885.

system by the CCl_2 group. The calculations for 1,1-dichloro-2-p-chlorophenyl-2-methylcyclopropane, 1,1-dichloro-2-p-tolylcyclopropane, and 1,1-dichloro-2-mesitylcyclopropane are summarised in Figure 2 wherein the variation in $_mK$(calc.) with angles of rotation $0° \leqslant \phi \leqslant 180°$ is shown for each case. Also included in
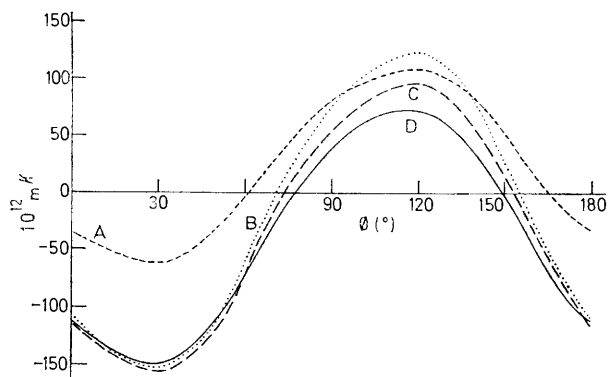

FIGURE 2   Plot of $10^{12}{_mK}$ against ϕ for A, 1,1-dichloro-2-p-tolylcyclopropane; B, 1,1-dichloro-2-mesitylcyclopropane; C, 1,1-dichloro-2-p-chlorophenyl-2-methylcyclopropane; and D, 1,1-dichloro-2-p-chlorophenylcyclopropane

Figure 2 are the corresponding calculations for 1,1-dichloro-2-p-chlorophenylcyclopropane for which Le Fèvre et al.[5] had reported an experimental $_\infty(_mK_2)$ in CCl_4 of -104×10^{-12} though they did not attempt a theoretical interpretation of this datum.

From Figure 2 we see that accord between theoretical molar Kerr constants and those from experiment is achieved when ϕ equals 53 or 177° for 1,1-dichloro-2-p-chlorophenylcyclopropane, 60 or 166° for 1,1-dichloro-2-p-chlorophenyl-2-methylcyclopropane, 65 or 160° for 1,1-dichloro-2-p-tolylcyclopropane, and 76 or 150° for 1,1-dichloro-2-mesitylcyclopropane. Examination of scale molecular models shows clearly that, in each case, the larger ϕ value describes a conformation which is precluded on steric grounds. This is indicated also by calculation using the appropriate geometric parameters from refs. 4 and 19 and standard van der Waals radii.[22] Our conclusions are summarised in Table 2 together with the results of previous work from ref. 5.

A
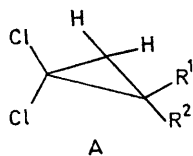
The mean value of ϕ for the five 1,1-dichloro-2-phenylcyclopropanes is 60° ($\pm5°$ standard deviation). This is larger than the estimate of 30° reported by Arbuzov et al.[23] for 1,1-dichloro-2-phenylcyclopropane. If the ortho-hydrogen atoms of the phenyl are replaced by methyl groups the steric deflection by the chlorine

[22] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, New York, 3rd edn., p. 260.
[23] B. A. Arbuzov, A. N. Vereshchagin, and S. G. Vul'fson, Izvest. Akad. Nauk S.S.S.R., Ser. Khim., 1972, 21, 461.

atoms is greater and the angle of rotation ϕ rises to ca. 76°. The degree of conjugative interaction between the

TABLE 2

Preferred solution-state conformations of molecules A

R^1	R^2	Solvent	ϕ (°)	Ref.
Ph	H	CCl_4	56 *	5
Ph	Me	CCl_4	65	5
p-ClC_6H_4	H	CCl_4	53	Present work
p-ClC_6H_4	Me	C_6H_{12}	60	Present work
p-MeC_6H_4	H	C_6H_{12}	65	Present work
Mesityl	H	C_6H_{12}	76	Present work

* From curve A of Figure 3 in ref. 5.

phenyl and cyclopropyl ring systems is progressively lowered as ϕ increases though it has been shown by Bernett[1] that, on the basis of the bent bond model for bonding in cyclopropane, overlap between sp^5 hybrid orbitals with the p orbital of an adjacent aromatic carbon atom is appreciable even for ϕ as large as 60°.

In the case of 1,1-dichloro-2,2-diphenylcyclopropane the variation of $_mK$(calc.) with angles of rotation ϕ is shown in Figure 3. The unbroken curve refers to the symmetric case in which each phenyl ring is rotated by
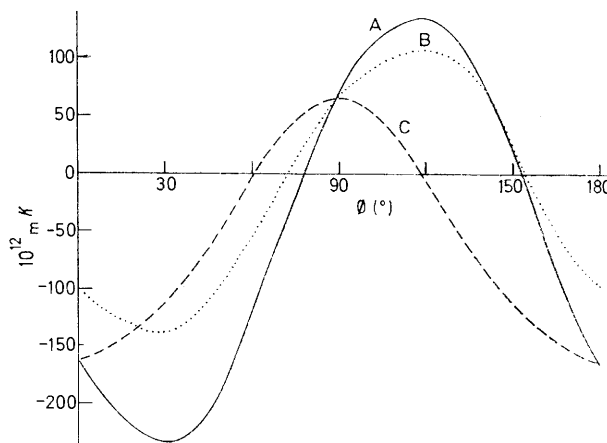

FIGURE 3   Plot of $10^{12}{_mK}$ against ϕ for A and C, 1,1-dichloro-2,2-diphenylcyclopropane; and B, 1,1-dichloro-2,2-dimethyl-3-phenylcyclopropane

the same angle ϕ away from the CCl_2 grouping while the broken line applies to (equal) rotations ϕ in which one phenyl ring is rotated away from the CCl_2 group and the other phenyl ring is rotated towards it. Four values of ϕ are theoretically allowable but of these only $\phi = ca.$ 70° (symmetric) corresponds to a sterically permissible conformation. De Lacy and Kennard[24] have recently reported an X-ray structure analysis for 1,1-dichloro-2,2-bis-p-chlorophenylcyclopropane; they show that each aromatic ring has a disposition ϕ of ca. 80° in the solid state configuration.

Finally we consider 1,1-dichloro-2,2-dimethyl-3-phenylcyclopropane for which theoretical $_mK$ values are plotted against ϕ in Figure 3. The contribution of the C(cyclopropyl)Me_2 group to the overall molecular

[24] T. P. De Lacy and C. H. L. Kennard, J.C.S. Perkin II, 1972, 2141.

polarisability anisotropy is uncertain. An attempt was made to extract an estimate of this from measurements on the model compound 1,1-dichloro-2,2,3,3-tetramethyl-cyclopropane. The observed molar Kerr constant $(43\cdot6 \times 10^{-12})$ when analysed in terms of the permanent electric moment $(2\cdot43$ D) and the cyclopropane, C–H, and C–Cl group polarisabilities quoted earlier, leads to a near equal polarisability contribution of the two CMe_2 groups along the X,Y,Z directions. This was assumed also to be the case with the CMe_2 group in 1,1-dichloro-2,2-dimethyl-3-phenylcyclopropane. Two conformers are theoretically possible with ϕ $ca.$ 100 or alternatively $ca.$ 134°. The former value is preferred since it corresponds to a conformation which is much less hindered sterically than the latter.

Hexabromocyclopropane Polarisabilities.—The principal polarisability semi-axes of hexabromocyclopropane may be derived from the experimental molar Kerr constant and the electron polarisation $_EP$ using equations (1) and (2) [8] since, for this molecule, $b_1 = b_2 \neq b_3$ where b_3 is located along the three-fold symmetry axis. The

$$_mK = 4\pi N_D P(b_1 - b_3)^2/405kT_EP \qquad (1)$$

$$_EP = 4\pi N(2b_1 + b_3)/9 \qquad (2)$$

term $_DP$ is the distortion polarisation which equals the measured $_\infty P_2$ (64·7 cm³). In the absence of relevant refractivity dispersion data we assume that $_EP = 0\cdot95R_D = 58\cdot1$ cm³. Solution of the equations leads to two mathematically possible sets of b_i values: $b_1 = b_2 = 25\cdot02$, $b_3 = 19\cdot17$, or, alternatively, $b_1 = b_2 = 21\cdot12$, $b_3 = 26\cdot97$. From these molecular parameters can be derived estimates of the polarisability semi-axes of the C(cyclopropane)–Br bond by a procedure similar to that used in ref. 5 to specify the C(cyclopropane)–Cl polarisabilities. The Br–C–Br angle was assumed to be 112° by analogy with the corresponding Cl–C–Cl and F–C–F bond angles.[19,25,26] Two sets of C(cyclopropane)–Br bond data emerge: $b_L(C–Br) = 2\cdot65$, $b_T(C–Br) = b_V(C–Br) = 4\cdot04$, corresponding to $b_1(C_3Br_6) > b_3(C_3Br_6)$, and, alternatively, $b_L(C–Br) = 5\cdot09$, $b_T(C–Br) = b_V(C–Br) = 2\cdot82$ when $b_1(C_3Br_6) < b_3(C_3Br_6)$. The $b_L(C–Br) : b_T(C–Br)$ ratios are respectively 0·66 and 1·80; the latter alone is of the order of magnitude expected for a C–Br bond from previous determinations of C–Br polarisabilities in a variety of molecular environments (see Table 22 on p. 50 of ref. 12 and p. 4936 of ref. 11). Thus we deduce that the C(cyclopropane)–Br bond semi-axes are best specified as $b_L(C–Br) = 5\cdot09$, $b_T(C–Br) = b_V(C–Br) = 2\cdot82$ and these values are used in the subsequent calculations.

Conformations of 2-Aryl-1,1-dibromocyclopropanes.—

The procedure is analogous to that used for the dichloro-derivatives. The following additional polarisability data are required: $b_L(C_{ar}–Br) = 6\cdot3$, $b_T(C_{ar}–Br) = 2\cdot5$, $b_V(C_{ar}–Br) = 2\cdot2$.[17] The Br–C–Br angle was retained as 112° throughout. The dipole moment vectors of 1,1-dibromo-2-phenylcyclopropane and of 1,1-dibromo-2,2-diphenylcyclopropane (1·89 and 1·84 D respectively) were located along the bisector of the CBr_2 angle. With 1,1-dibromo-2-p-tolylcyclopropane and 1,1-dibromo-2-p-bromophenylcyclopropane the moment directions were derived vectorially on the basis that μ(observed) is composed of μ(1,1-dibromo-2-phenylcyclopropane) and a second vector component directed along the phenyl 1,4-axis. The theoretical molar Kerr constants thus obtained were compared with the appropriate experimental values of Table 1; accord was achieved when $\phi = 72$ or 158° for 1,1-dibromo-2-phenylcyclopropane, 67 or 149° for 1,1-dibromo-2-p-tolylcyclopropane, 61 or 168° for 1,1-dibromo-2-p-bromophenylcyclopropane. As in the case of the chloro-analogues, the larger ϕ estimates correspond to structures which are precluded on steric grounds. The mean value of ϕ for the three 1,1-dibromo-2-phenylcyclopropanes is 67 ($\pm6°$); this is appreciably larger than that (40°) reported for 1,1-dibromo-2-phenylcyclopropane by Arbuzov *et al.*[23] The apparent small difference in the conformational parameter ϕ between the dichloro- and the dibromo-phenyl-cyclopropanes is probably not related to the size of the halogen as the phenyl ring does not occupy space adjacent to either the Cl or Br group when ϕ is of the order of 60°. Most likely the phenyl group is deflected by the *cis*-halogen atom away from the resonance favoured bisected disposition ($\phi = 0°$) and it is, in turn, further rotated through steric interaction between the phenyl *ortho*-hydrogen atoms and the (cyclopropyl) methylene group. Finally we note that for 1,1-dibromo-2,2-diphenylcyclopropane four values of ϕ are theoretically possible from analysis of the molar Kerr constant: 69 or 161° (symmetric) and 46 or 134° (asymmetric). The ϕ (symmetric) estimate of 69° alone is sterically reasonable and agrees closely with the conformation [*ca.* 70° (symmetric)] for 1,1-dichloro-2,2-diphenylcyclo-propane.

[25] P. P. Barzdain, N. I. Gracheva, and N. V. Alekseev, *Zhur. Strukt. Khim.*, 1972, **13**, 717.
[26] J. F. Chiang and W. A. Bernett, *Tetrahedron*, 1971, **27**, 975.