Substituent-induced Asymmetry of the Cyclopropane Ring

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Summary Analysis of the planar moments of cyclopropyl derivatives studied by microwave spectroscopy indicates a consistent shortening of the C–C bond opposite an unsaturated substituent compared with the corresponding length opposite saturated substituents.

While about 20 cyclopropane derivatives have been studied by microwave spectroscopy, very few conclusions regarding ring bond lengths in these compounds have resulted. Interaction between substituent groups and the cyclopropyl ring could alter the equilateral symmetry of the parent hydrocarbon. Hoffman, for example, has suggested[1] that conjugation between unsaturated substituents and the extra-annular molecular orbitals of the ring should effect an increase and decrease in the bond lengths adjacent and opposite, respectively, to the substituent.

Schwendeman and Jacobs[2] have shown by the isotopic substitution method that in cyclopropyl chloride the ring is nearly equilateral with bond lengths 1·515 ± 0·001 and 1·513 ± 0·004 Å opposite and adjacent respectively to the substituent. For this cyclopropane derivative as well as a number of others studied, the ring C–C bond is bisected by a plane of symmetry and the substituent atoms lie within this symmetry plane. For this class of compounds, neglecting zero point vibrational effects, the planar moment, P_{zz}, associated with the symmetry plane is given by equation (1),

$$P_{zz} = 4m_{\mathrm{H}}z_{\mathrm{H}}^2 + 2m_{\mathrm{C}}z_{\mathrm{C}}^2 \qquad (1)$$

and small changes in P_{zz} approximately by equation (2),

$$P_{zz} - P^0{}_{zz} = 8m_{\mathrm{H}}z^0{}_{\mathrm{H}}\,(z_{\mathrm{H}} - z^0{}_{\mathrm{H}}) + 4m_{\mathrm{C}}z^0{}_{\mathrm{C}}\,(z_{\mathrm{C}} - z^0{}_{\mathrm{C}}) \qquad (2)$$

in which m_{H}, m_{C}, z_{H}, and z_{C} are the masses and out-of-plane co-ordinates of the ring hydrogen and carbon atoms opposite the substituent (z_{C} is one-half the C–C bond length opposite the substituent). Assuming that the H and C co-ordinates change by the same amount, equation (3)

$$r\,(\text{Å}) = 1{\cdot}515 + 4{\cdot}29 \times 10^{-2}\,[P_{zz}\,(\text{a.m.u.Å}^2) - 20{\cdot}34] \qquad (3)$$

relates this bond length to the planar moment, taking the co-ordinates and moments of cyclopropyl chloride as a reference. From equation (3) and the reported planar moments of cyclopropanone[3] and methylenecyclopropane,[4] the latter being corrected for contributions of the out-of-plane methylene hydrogens, the C–C bond lengths are calculated to be 1·575 and 1·538 Å respectively. These compare well with r_s values of 1·575 ± 0·009 and 1·5415 ± 0·0003 Å, respectively.

TABLE

Substituent	Planar moments (a.m.u. Å^2)[a] Uncorrected	Corrected[b]	Bond length (Å)
Group I			
Me	21·82[c]	20·22	1·510
CH_2Cl *cis*	20·95[d]	19·35	1·473
Cl	20·34[e]	20·34	(1·515)
Cl_2	20·39[f]	20·39	1·517
Br	20·18 ± 0·20[g]	20·18 ± 0·2	1·508
NH_2	21·55[h]	20·21	1·509
ND_2	22·89[h]		
PH_2	22·18[i]	20·03	1·502
PD_2	24·32[i]		
Group II			
$CHCH_2$ *trans*	19·97[j]	19·97	1·499
CHO *cis*	19·76[k]	19·76	1·490
CHO *trans*	19·92[k]	19·92	1·497
CFO *cis*	19·76[l]	19·76	1·490
CFO *trans*	19·81[l]	19·81	1·492
CO_2H *cis*	19·80[m]	19·80	1·492
COMe *cis*	21·31[n]	19·71	1·488
NO_2	19·99[o]	19·99	1·500
CCH	19·94 ± 0·03[p]	19·94 ± 0·03	1·498
CN	19·98[q]	19·98	1·500

[a] Experimental uncertainties ±0·01 a.m.u. Å^2 except where noted. [b] Methyl group correction, −1·60 a.m.u. Å^2; amine and phosphine correction deduced from isotopic data. [c] R. G. Ford and R. A. Beaudet, *J. Chem. Phys.*, 1968, **48**, 4671. [d] F. Ito, J. C. Chang, and H. Kim, Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1971, paper B8. [e] R. H. Schwendeman, G. D. Jacobs, and T. M. Krigas, *J. Chem. Phys.*, 1964, **40**, 1022. [f] W. H. Flygare, A. Narath, and W. D. Gwinn, *J. Chem. Phys.*, 1962, **36**, 200. [g] F. M. K. Lam and B. P. Dailey, *J. Chem. Phys.*, 1968, **49**, 1588. [h] D. K. Hendricksen and M. D. Harmony, *J. Chem. Phys.*, 1969, **51**, 700. [i] L. A. Dinsmore, C. O. Britt, and J. E. Boggs, *J. Chem. Phys.*, 1971, **54**, 915. [j] E. G. Codding and R. H. Schwendeman, Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1968, Paper N6. [k] H. N. Volltrauer and R. H. Schwendeman, *J. Chem. Phys.*, 1971, **54**, 260. [l] H. N. Volltrauer and R. H. Schwendeman, *J. Chem. Phys.*, 1971, **54**, 268. [m] J. Sheridan, Fourth Austin Symp. on Gas Phase Molecular Struct., Austin, Texas, 1972, paper W9. [n] P. L. Lee and R. H. Schwendeman, Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1969, paper U8. [o] A. R. Mochel, C. O. Britt, and J. E. Boggs, unpublished results. [p] M. J. Collins, C. O. Britt, and J. E. Boggs, *J. Chem. Phys.*, in the press. [q] R. E. Penn and J. E. Boggs, unpublished results.

In the Table, the planar moments, corrected where necessary for contributions of out-of-plane substituent hydrogens, and C–C bond lengths calculated from equation (3) are given for all the symmetrical cyclopropane derivatives reported to date. With the exception of *cis*-chloromethylcyclopropane, the indicated bond lengths of the unsaturated derivatives in Group II are consistently less than those of the saturated derivatives in Group I by an average of 0·015 Å. This trend parallels the *X*-ray crystallographic observation that the cyclopropane bond lengths in the fused-ring system 2,5-dimethyl-7,7-dicyanonorcaradiene[5] are 1·554 and 1·559 Å adjacent to the cyano-groups and 1·501 Å opposite the cyano-groups.

The most likely alternative explanation of the observed trend in the planar moments might be a consistent trend in the zero-point vibrational contributions. Two considerations argue against this objection. First, correction for the expected low-frequency out-of-plane bending mode of molecules in Group II of the Table produces a change which is not only too small to affect the results appreciably, but is also in the wrong direction so that the differences in the Table would be slightly accentuated. Second, a rough estimate of the zero-point vibrational effects can be obtained by subtracting in each case the planar moments of the corresponding vinyl compound. This procedure changes the predicted bond lengths in the Table by an average of only 0·0017 Å, again very slightly accentuating the difference between the two groups.

The indicated short ring bond for *cis*-chloromethylcyclopropane is not accounted for by the unsaturated substituent model, but may be by invoking *d*–π overlap with the ring MOs.

While the considerations presented here can give no indication about the lengths of the C–C bonds adjacent to the substituent, they do indicate consistent interactive effects on the lengths of the opposite bond and are highly suggestive of ring asymmetry.

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