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RING STRAIN AND THE NEGATIVE POLE—I

EVALUATION OF THE POLE, AND ITS APPLICATION TO THE CALCULATION OF ELECTRIC MOMENTS

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Abstract—A separation of the total charge in strained bonds into two components is postulated; the bulk of the charge leading to normal properties, and a small fraction reflecting the "deviations". From the ring bending strain energy, the magnitude of the pole is calculated, and this pole gives calculated electric moments for several compounds in good agreement with experiment. An empirical formula for calculating the ring bending strain is also offered.

ALTHOUGH the concept of strain has been used for a considerable time to explain qualitatively the ease of forming and breaking strained systems, it seems that almost no attempts have been made to investigate the possibility that a strained system might have unusual electronic effects *as a consequence of that strain.* Quantum mechanics indicates that if the ψ-function for a molecule can be determined, then appropriate operators allow the calculation of any given property. If all the properties can be linked to one function, then it should follow that a change in one property from an expected standard (in this case, the energy of the system) will be reflected by corresponding changes in *all* properties linked to that function. Since these effects have not been realized, other concepts, especially conjugation, have been invoked to explain the unusual properties of strained systems. It is the purpose of this series of papers to investigate whether any of the unusual properties of small rings can be interpreted, either partially or wholly, in terms of strain, and if the former, to what degree.

In the Born–Oppenheimer approximation, chemical binding energy is the sum of several electron energy terms, together with a term for the internuclei interactions. Since the object is to relate molecular properties with strain, it is convenient to divide the total charge into two charges, q' and q so that the contributions of q' to all the electronic terms plus the total of the internuclear interactions sum to zero. Now the total strain can be considered as the work done (W) in assembling the charge q on the "normal standard molecule" of identical geometry. In terms of the wave function, this division can be expressed as

$$\int \psi_q \cdot \psi_q^* \, d\tau + \int \psi_{q'} \cdot \psi_{q'}^* \, d\tau = \int \psi \cdot \psi^* \, d\tau = \text{total electrons} \quad (1)$$

where

$$\int \psi_q H \psi_q^* \, d\tau = \text{strain energy} \quad (1a)$$

$$E'nn + \int \psi_{q'} H \psi_{q'}^* \, d\tau = \text{standard "unstrained" energy} \quad (1b)$$

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and

$$E'nn + \int \psi H \psi^* \, d\tau = \text{observed energy} \tag{1c}$$

Thus any observable property of the system should be calculable by adding the contributions of q to q' in the same way that the total energy can be obtained by adding 1a to 1b if no other effect is present.

The Hellmann–Feynman theorem[1] shows that the extremely complex electrodynamical problems of chemical bonding can be reduced to a more simple problem of electrostatics—the nuclei are considered as embedded in an electrostatic matrix, the density at any point being proportional to the probability of finding an electron there. If the bonds can be represented as an electrostatic distribution, and work is done on the bonds, and since

$$W = \frac{Q^2}{2C} \tag{2}$$

and only initial and final states are considered, then an associated charge *must* be generated by the work done. Thus several properties of strained molecules should reflect q, and superficially this seems to be true. Thus strained hydrocarbons are attacked by electrophilic reagents far more rapidly than normal hydrocarbons, and the more strain the greater the rate, as is shown by comparing the reactivities of the cyclopropane bond and the bridgehead bicyclobutane bond.[2]

To obtain q from Eq. (2), W and C have to be evaluated. W can be identified as the ring bending strain energy. Unfortunately, strain measured experimentally is a composite factor, consisting of substituent eclipsing strain, torsional strain, strain between atoms closer than the sum of their Van der Waals radii, and ring bending strain. These effects have been analysed in detail for cyclobutane[3] and cyclopentane.[4] Furthermore, when the bond angles are bent sufficiently it is also found that bonds to adjacent substituents are strengthened, making the compound appear less strained. This can only be corrected for by having an accurate knowledge of the changes in the strengths of these bonds. An analysis of this effect has been done for double and triple bonds,[5] these being regarded here as 2 membered and two fused 2 membered rings, and these data show a considerable strengthening of adjacent bonds, a strengthening which increases with increasing ring strain. If the double bond can be thought of as a 2-membered ring, a strengthening of adjacent bonds might be expected for 3-membered rings, and indeed force constants indicate that this is so.[6] As further expected, the effect is almost unobservable for cyclobutane.[4] Similarly it might be thought that eclipsing strain, which could account for up to 8 Kcals/mole in cyclobutane,[3] might also be present in cyclopropane. Since this will tend to be cancelled by the bond strengthening effect, it might be expected that the total strain of cyclopropane is very close to the ring strain.

A different opinion has been expressed[7] from considerations of activation energies. Thus the activation energy for breaking a cyclopropane ring is 9 Kcals/mole less than the total strain,[7a] while the activation energy for the cyclization of the trimethylene diradical is approximately 8 Kcals/mole.[7b] This was interpreted as evidence that the eclipsing energy in the transition state was 8–9 Kcals/mole, and hence the ring strain for cyclopropane was about 19 Kcals/mole rather than the total strain of 28 Kcals/mole. However, an alternative view is considered here to be more probable. In the transition state for both these reactions, the geometry must be close to the cyclopropane geometry, and this implies that one C—C—C angle must be fairly close to its final value of 60°—this must be so just as much for the eclipsing explanation as for this—and since it is not taking any part in the bond making or breaking, it follows that approximately one third of the cyclopropane ring strain should be present in the transition state. If this is so, then the activation energy of 9 Kcals/mole mentioned above is quite reasonable evidence that the ring strain of cyclopropane is close to its total strain.

The possible form of an empirical relationship for calculating W might be deduced from the location of q in each bond. A possible location would be at the intersection of the unstrained orbital axes, as more elaborate calculations[8] indicate that bent bonds only deviate a few degrees from the tetrahedral bonds, and since q' is the bulk of the charge and makes compensation for internuclear effects, q should be further from the internuclear axis than q'. This would allow each pole to develop at constant distance from its neighbouring poles, and thus avoid second order electron repulsion terms. The validity of this assumption would rest in the possibility that the strain can be represented as a first order function of the angle through which the bonds are bent (θ). It must equal zero when $\theta = 0$, and reach a maximum when $\theta = 180°$, and empirically the best function is sin $\theta/2$. After empirically correcting for alteration of bond lengths, a simple relation is

$$W = \frac{nk \sin \theta/2}{\sqrt{r}} \tag{3}$$

k is a constant for carbon equal to 19·2 Kcals/mole^{-1} angstrom$^{-\frac{1}{2}}$
n is the number of junctions
r is the bond radius for the atom considered.

For carbon, the unstrained angle is generally the tetrahedral angle, but if there are two junctions on one carbon, the presence of one ring may lead to angles greater than 109°. In this case, θ with and without the other junction is calculated, and the average used if the two junctions are equivalent. Otherwise relative corrections are estimated. A junction is a pair of equal bond repulsions. Thus ethylene has two junctions, and acetylene four, not six. A junction is formed when an orbital is bent to form a bond, and when two orbitals are bent to form the triple bond in acetylene, two junctions are formed.

Table 1 contains some strain energies calculated from equation 3. The geometrical factors assumed are exo bond angles of 109° for cyclobutane, 114° for cyclopropane, and 120° for ethylene. Experimentally determined bond lengths are used where known, otherwise estimated values are used.

Comparing the calculated and experimental values, it is felt that this formula does give a good indication of the ring strain present, especially for 2 and 3-membered rings. For the larger rings, as mentioned before, the situation is more complex because of the larger number of effects present, but if eclipsing energies include the eclipsing of non-adjacent bonds in 4-membered rings such as cyclobutane and cubane, the calculated strains at least seem reasonable. Furthermore, if the formula is assumed correct, small discrepancies can be interpreted as due to other causes, and reasonable values for them can be calculated.

TABLE 1. STRAIN ENERGIES OF COMPOUNDS IN Kcals/mole

Compound	Ring strain calculated from Eq. 3	Calculated total strain from Ref. 9	Experimental strain	References and comments
Ethylene	38·4	—	38·7	5
Acetylene	83·3	—	83·1	5
Allene (ave middle)	79·0	—	80·5	*k*
(no ave)	80·1			
Cyclopropane	27·3	31	27·5	*a*
Cyclobutane (planar)	14·7	—	26·2	*b*
Cyclobutane (puckered)	17·3	—	26·2	*b*, *c*
Cyclopentane (puckered)	3·31 0·339	—	ring strain from force constants −3·6	2, *d*, *e*
Cyclopropene	71·8	72·24	52·6	*a*, *g*, *h*
Cyclobutene	57·4	—	56·31	*g*, *f*
Cyclobutadiene	100·1	—	—	*g*
Bicyclobutane	58·5	67·4	64–67, 63·7	*i*, *f*
Tetrahedrane	97·2	150·5	—	
Cubane	57·3	—	—	
Triprismane	84	—	—	
Spiropentane	56	75·2	61·4	*j*
Methylenecyclopropane	67	62·24	66·8	*f*
Dimethylenecyclopropane	106·8	91·8		
Trimethylenecyclopropane	146·6	118·46		
Methylenecyclopropene	110·4	96·54		
Methylenecyclobutane	54	—		
1,3-dimethylenecyclobutane	92·5	—		
Spiropentadiene	144·8	151·36		
Bicyclo(110)butadiene (Planar, all C—C = 1·483)	146	102·66		

[a] H. A. Skinner and G. Pilchard, *Quart. Revs.* **17**, 264 (1963).

[b] G. Kaarsemaker and J. Coops, *Rec. Trav. Chim.* **71**, 261 (1952).

[c] Angles assumed 86·5.

[d] Angles assumed 106°.

[e] Value 0·339 is calculated from the electric moment of cyclopentyl chloride and corresponds to an average internal angle 22′ less than the tetrahedral angle. This discrepancy might indicate that either there is a partly cancelling +ve pole, or that the internal angle is larger than might be thought from the entropy data.

[f] Calculated from application of bond strengths in reference 5 to heats of combustion measured by K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.* **90**, 3395 (1968).

[g] No averaging of angles as non equivalent bonds.

[h] In experimental value, no account was taken of the double bond as a strained system, nor of adjacent stabilization. Approx. 20 Kcals should be added.

[j] F. M. Fraser and E. J. Prosen, *J. Res. Nat. Bur. Stds.* **54**, 143 (1955).

[i] K. B. Wiberg, *Records of Chemical Progress* **26**, 143 (1965). But Ref. 8 quotes a value fo 62·8 for the 1,3-dimethyl derivative.

[k] Calculated from application of bond strengths in ref. 5 to heats of hydrogenation measured by G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *J. Am. Chem. Soc.* **58**, 146 (1936).

Thus if spiropentane is considered as approximately two cyclopropane rings, and if it is assumed that the eclipsing energy equals the stabilization energy in cyclopropane, an estimate of these energies can be made. Compared with two cyclopropane rings, the total eclipsing energy should be very similar since the eclipsing energy of the C—H bonds of one ring with the C—C ring bonds of the other rings should be similar to the corresponding eclipses on a cyclopropane ring. If these are equal, then the experimental strain energy will be higher than the ring-strain by the stabilizing energy of the four missing C—H bonds. This leads to the conclusion that the C—H bond on a cyclopropane ring is stabilized by approximately 1·4 Kcals/mole, which is at least a reasonable value.

Recently some SCF MO calculations have been published on strain energies.[9] Since these calculations do not consider the double bond as a strained ring, for comparison strain energies have been calculated from their calculated heats of atomization and the bond energies in Ref. 5. In general, the agreement between the SCF calculations, the present calculations, and experiment is quite good for simple compounds. The agreement between the present calculations and the SCF calculations is not as good for unsaturated compounds, especially for bicyclo(110) butadiene, and for more highly strained compounds, especially tetrahedrane. The SCF calculations indicated that tetrahedrane would be converted to the bicyclobutane biradical almost thermo-neutrally; while these calculations indicate that such a conversion should require, neglecting small differences in the stability of a radical on a secondary carbon, 46 Kcals/mole, which implies that tetrahedrane could possible be made.

Since Eq. 3 is an I-strain formula, it differs from the SCF calculations on the addition of methylenes to a cyclopropane ring, but delocalization energies and bond stabilizations have not been taken into account here, and this presumably will account for some of this difference. And in as much as Eq. 3 gives good values for ethylene and acetylene where displacements are large, and for cyclopropane and cyclobutane, where displacements are small, it is felt that Eq. 3 at least gives a reasonable value for the ring strain. Unfortunately there are insufficient data for further testing this equation—even the cyclopentane value is not very applicable, since the mean angle can only be estimated. However, the values thus obtained, since they do agree quite well with experimental values, should be accurate enough to obtain a reasonable value for q from Eq. 2.

Evaluating the capacity of the molecule presents the same difficulties for an exact solution as does the full quantum mechanical analysis, since the exact distribution of charge must be known—the capacity of the frame is not the same as if the frame were a conductor, since the potential is not constant over the molecule. However, approximations can be made, and since most of the molecules considered are of the same order of dimensions, thus giving capacities of similar magnitude, any approximate formula empirically set for one structure should give reasonable values for the rest. Furthermore, since Eq. 2 only requires the square root of the capacity, resultant errors from the approximation should be minimized.

The capacity will be proportional to the distance of q from the centroid, and this will be the major cause of variation. The other factors influencing the capacity will be geometric shape and charge distribution within the individual bonds, but since all the compounds are about the same size, and since the bent bonds should offer approximately the same shaped frame for q in each of the compounds, these factors might just as well be incorporated in the constant of proportionality. Thus the capacity is given by the formula

$$C = kr \tag{4}$$

Empirically, $k = 8\ \varepsilon_0$, which is identical to the constant for a planar disc.

Since Eq. 3 suggests the strain is proportional to the number of junctions, the capacity of 2 fused rings can be considered as the sum of the individual capacities, at least as long as the bridgehead bond can be considered as being under potential repulsion from the remainder of the system. Thus, apart from differences in bond distances, the triple bond would have twice the capacity of a double bonded system. Extending the analogy of the triple bond, it is suggested that the capacity of a three dimensionally strained compound such as tetrahedrane or cubane would be given by twice that from equation 4, since each carbon can be considered as a less strained version of the acetylenic carbon. Unfortunately there is no experimental evidence to indicate the accuracy of this assumption. This would also suggest that the capacity of two fused systems would be the sum of the individual capacities, to the first approximation, since equation 3 treats each section independently. As is shown below, this assumption is consistent with experimental evidence, where it is available.

A further complication in the case of 4-membered rings is the 1–3 non-bonded interaction between nuclei. This presumably arises because the nuclei are sufficiently close that they no longer appear electrically neutral to each other. Since this form of strain is very much similar to the ring strain being considered, and since the nuclei are more likely to see each other as positive centres, this type of strain will, by similar reasoning, give rise to a positive pole and this will tend to cancel some of the effects of the negative pole. Since the negative pole is being considered as arising from 4 contributing point sources, capacities for the positive pole have also been calculated for cyclobutane.

Spiro compounds provide a further difficulty, but since there are almost no data in the literature to compare with any predictions these will not be discussed further.

Table 2 gives capacities for some compounds, calculated from the above formulae, and the magnitude of the negative pole, Σq, based on this capacity. Since these poles

TABLE 2. CAPACITIES AND NEGATIVE POLES

Substance	Capacity 10^{22} F	−ve Pole (in fractions of electronic charge)
Ethylene	67·4	0·374
Acetylene	132·8	0·774
Cyclopropane	56·2	0·288
Cyclobutane (planar)	64·7	0·227
Cyclobutane (+ve)	78·0	−0·146
Cyclobutane (total)	—	0·078
Bicyclobutane	115·9	0·604
Tetrahedrane	156·4	0·903
Cubane	196	0·780
Cubane (+ve)	191	−0·513
Cubane (total	—	0·267
Cyclopentane	77·9	0·038 (obtained from electric moment of cyclopentyl chloride)

are based on an assessment of strain energies, and on capacities, either or both of which may be in error, the calculated values must be regarded as only approximate, but since the magnitude of q depends only on the square root of these quantities, the errors should not be too great, and the calculated poles should be capable of yielding predictions of the properties of molecules with sufficient accuracy at least to make some check on the validity of the original hypothesis.

One application of the above ideas is the calculation of electric moments of strained molecules. It should be noted that approximate agreement between experimental and calculated values is not sufficient to prove the theory, because the capacity constant is chosen to obtain as good agreement as possible. However, consistently good agreement over a number of different molecules should lend general support to the theory, since only one constant is used to relate the electric moment to the geometry and the strain energy of the molecule—quantities that are clearly related on electrostatic arguments, which by the Hellmann–Feynman Theorem should apply.

Qualitatively it is observed that if a strained ring is placed adjacent to a bond, the electric moment changes in such a way that the strained section appears more negative than is expected for a carbon skeleton. For halide derivatives, this is usually explained in terms of conjugation between lone pair electrons and p orbitals on the strained ring. Thus electric moment measurements have been taken as evidence that cyclopropane, and to a lesser extent, cyclobutane, can conjugate with adjacent lone pairs, although to a lesser extent than ethylene can.[10]

This theory is simple and seems quite adequate, but some small points are not immediately clear. Thus although alkyl chlorides generally have lower electric moments than alkyl bromides (ethyl chloride 1·98D, ethyl bromide 2·01D, n-propyl chloride 2·04D, n-propyl bromide 2·15D[11]), cyclopropyl bromide has a lower dipole moment than cyclopropyl chloride (1·69D and 1·76D) and the same order is sound for the ethylene halides (1·415D and 1·449D) and the acetylene halides (ca. 0D and 0·446D). Yet chlorine is generally considered a better conjugating group.

Another problem arises in the case of the halobenzenes. The benzene ring is supposedly a good conjugating group, yet bromobenzene and chlorobenzene both have dipole moments of approximately 1·70D, which is approximately the same as the corresponding cyclopropyl compounds. This is extremely surprising, especially when it is remembered that conjugation to the para position markedly increases the charge *separation* compared with conjugation to a β carbon in ethylene or cyclopropane, and furthermore, since the para position lies on the C—X bond line, consideration of vector subtraction shows this position to be the most efficient for lowering the resultant moment. Thus on the conjugation theory, it would appear that very little charge is actually relayed to the *para* position, for which there seems to be no obvious explanation.

The conjugation theory also does not explain easily why an alkyl substituent should give a resultant electric moment on a small ring system. Hyperconjugation postulates that saturated bonds can act as "pseudo lone pairs" and give a conjugative effect, but it is not obvious why the effect is so large. Thus in propene, the methyl must conjugate at least half as well as a chlorine to give an electric moment of 0·34D, and double its conjugating power to give an electric moment of 0·75D for propyne, which is especially surprising since it is generally believed that the triple bond does not conjugate markedly better than the double bond.

Some of these problems can be accounted for in terms of the negative pole q. Since q' was interpreted as leading to "normal" properties, the electric moment of a strained molecule can be considered as its "normal" electric moment together with a further moment due to the monopole q. In a symmetrical carbon skeleton, the negative pole will be at the centre of the strained system, and there will be no resultant moment. If one substituent is added, the negative pole is no longer at the centre of the system, and to the dipole moment of that substituent bond must be added vectorially the moment of the pole charge times the displacement. When the substituents are arranged symmetrically there will naturally be no effect due to the negative pole, and if one substituent is replaced by another of the same size and position with respect to the rest of the molecule, again there will be no effect due to the negative pole.

However, if a symmetrical molecule has a bond replaced by one of different bond length, the negative pole will give rise to an electric moment given by

$$\mu = q \cdot \frac{\Delta r}{2} \tag{5}$$

where r is the radial distance from the negative pole to the substituents in the substitution considered. (For complete accuracy, r is a vector, but since the angle effects are small, this can be neglected generally.) Since most substitutions are concerned with the replacement of a hydrogen with another substituent, the strained small ring always has an apparent withdrawing effect when a bond moment is compared with a similar unstrained compound. The most obvious difference between this hypothesis and the conjugation theory is that this treatment postulates that the effect should be the same for equal bond lengths as long as there are no other effects superimposed, irrespective of whether there is a lone pair present or not. Thus it can be seen, without recourse to hyperconjugation, that propene should have a substantial electric moment, since the C—C bond is substantially longer than the C—H bond.

Before considering the results obtained from this hypothesis, it should be pointed out that there are certain factors which will cause the calculated values to be in error, and these are:

(a) It is convenient to neglect small angle differences. The general assumption is made that the bond angle on an ethylene carbon is 120°, 114° on a cyclopropyl and 111° on cyclobutyl carbon.

(b) It is convenient to assume that the bond moment of the hypothetical unstrained standard acts along the bond concerned. In general this will not be true, but there are usually insufficient data to correct for this, and in any case the difference is usually very small.

(c) Differing polarizabilities of bonds are neglected—again because there is no practical way of correcting for these.

(d) As the strain is increased, the ring atoms become more electronegative, and could cause a polarization of substituent bonds and lone pairs towards the ring. For the present this is neglected, except to point out that it should lead to an apparently greater withdrawing effect than calculated, and the effect should be most marked for the acetylenes.

(e) Since the resultant moment is found by subtracting a "strain moment" from the moment of the compound "without strain", it is important to decide as accurately as possible what this latter value would be. However, this itself is uncertain. For example, simple alkyl chlorides have electric moments ranging in value from 1·87D for methyl chloride to 2·17D for isopropyl chloride. While any choice of a standard is questionable, the standard for cyclopropyl is taken as the isopropyl analogue, for cyclobutyl and cyclopentyl, the cyclohexyl analogue is chosen (because all are puckered), for ethylene the corresponding ethyl compound is chosen, and for acetylenes the corresponding methyl compound.

In calculations, the strain moment is assumed to act along the line of the substituent and the negative pole. For an alkyl substituent, this is the direction of the final moment, and this has been determined for propene.[12] The experimental angle the moment makes with the bond axis is 17° or 33°, the two values because it is measured as two components, the direction of neither being known, while the calculated value is 17°36′.

For simple ring compounds where a substituent is attached to a symmetrical ring, the negative pole simply gives rise to a substituent effect, and some calculated values are compared with experimental values in Table 3. However, if the ring system is not symmetrical, then the negative pole q need not be at the centre of the ring, and simple hydrocarbon may itself have an electric moment. Three cases of this are illustrated below.

Bicyclobutane

The geometry is assumed to be that of two cyclopropane rings on planes at 120° to each other,[2] and the molecule is numbered so that the 1–3 bond is the bridgehead bond. It is further assumed that there is no non-bonded interaction between nuclei 2 and 4, the assumption being that the 1–3 bond will screen any positive potentials between these nuclei.

By symmetry, both the total negative pole Σq and the geometric centre are on the line of intersection of the two mirror planes through atoms 1–3 and 2–4. Let this line intersect the line joining atoms 1–3 at X. Then the geometric centre is at a distance 0·33A from X, and the point of intersection of the 1–3 tetrahedral axes, allowing for a final 1–3 bond distance at 1·48 Å, is 0·38 Å from X. Now the total pole is Σq of the individual bonds from earlier arguments and since q = C.V., the pole in each bond should be proportional to the potential applied by the remaining bonds. Now the bridgehead bond is under strain from four bonds, while the others are under potential interaction from two, thus the total pole is divided as

1	4	:	4	2
bond	potential		bonds	potential,

i.e. the bridgehead bond carried one third of the total pole. Since puckering a 4-membered ring without adding strain should not generate an electric moment, summing the poles of the four ring bonds will account for two thirds of the total pole, and will be centred at the geometric centroid. Thus a resultant moment is expected from the pole on the bridgehead bond of magnitude 0·68D. This compares well with an experimental value of 0·67D.[2]

The fact that the bridgehead bond carries one third of the negative pole also explains why the bridgehead bond is shorter and stronger than the others (if these

TABLE 3. ELECTRIC MOMENTS (IN DEBYE UNITS)

Compound	Assumed μ strainless	μ calculated	μ exp.	Method	Ref.
Methyl acetylene	0	0·75	0·75	Microwave	*a*
Fluoro acetylene	1·856	1·33	0·75	Microwave	*a*
Chloro acetylene	1·87	0·85	0·446	Microwave	*a*
Bromo acetylene	1·80	0·42	0		*b*
Iodo acetylene	1·60	−0·15	—		—
Propene	0	0·36	0·364	Microwave	*a*
Fluoroethylene	1·96	1·74	1·42	Microwave	*a*
Chloroethylene	2·00	1·49	1·42, 1·449	Microwave	*a*
Bromoethylene	2·03	1·40	1·415		*b*
Iodoethylene	2·05	1·31	1·30		*b*
Methyl cyclopropane	0	0·30	0·18 (ethyl)		*c*
Fluoro cyclopropane	1·96	1·79	—		
Chloro cyclopropane	2·15	1·75	1·76		*d*
Bromo cyclopropane	2·15	1·65	1·69		*d*
Iodo cyclopropane	2·15	1·54	—		—
Methyl cyclobutane	0	0·07	0·05 (ethyl)		*c*
Fluoro cyclobutane	1·96	1·94	1·94	Microwave	*a*
Chloro cyclobutane	2·20	2·10	—		
Bromo cyclobutane	2·20	2·07	2·09		*d*
Methyl cyclopentane	0	0·036	—		
Chlorocyclopentane	2·20	2·15	2·15		*b*
Methyltetrahedrane	0	0·94	—		
Chlorotetrahedrane	2·15	0·79	—		
Methyl cubane	0	0·27	—		
Chloro cubane	2·20	1·79	—		
Disubstituted compounds.					
1,1-Dichlorocyclopropane	2·25 (f)	1·57	1·58	Microwave	*a*
1,1-Dichloroethylene	2·07 (g)	1·29	1·34	Microwave	*a*
cis-1,2-Dichloroethylene	2·50 (h)	1·74	1·74		*e*
cis-1-Chloropropene	2·15	1·58	1·64	Microwave	*a*
trans-1-Chloropropene	2·15	1·99	1·97	Gas	*c*
2-Chloropropene	2·15	1·80	1·69	Gas	*e*
Iso-butylene	0	0·555	0·503	Microwave	*a*
cis-But-2-ene	0	0·507			

[a] Landolt Börnstein, *New Series*. Group II, Vol. IV, Springer-Verlag (1967).

[b] *Handbook of Chemistry and Physics* (46th Edition), The Chemical Rubber Publishing Company, E 57 (1965).

[c] Beilstein, Handbook of Organic Chemistry, 3rd Revision.

[d] M. Charton, *J. Chem. Soc.* 1205 (1965).

[e] *Handbook of Organic Structural Analysis* (Edited by Y. Yukawa) p. 500–509. Benjamin (1965).

[f] 2,2-Dichloropropane as standard.

[g] 1,1-Dichloroethane as standard.

[h] Estimated for 1,2-dichloroethane eclipsed from *cis*-1,2-dichlorocyclohexane, and correcting for the cyclohexane ring's usual exaltation twice. R. A. Oriana and C. P. Smyth, *J. Chem. Phys.* **17**, 1174 (1949) calculated the value for free rotation of 1,2-dichloroethane to be 2·46D.

properties are assumed proportional to the electron density in the bond) and at the same time why it is most susceptible to electrophilic attack.

Cyclopropene

There are three types of junctions in cyclopropene, which by equation 3 contribute the following strains:

(a) single-single 11 Kcals, (b) single-double 10·2 Kcals each, (c) double 20·2 each. Considering junction (b), since the single bond is under potential from two bonds and the combined double bond only from one, two thirds of (b) can be allotted to the single bonds, and one third to the double bond. Thus each single bond can be considered as contributing 12·3 Kcals/mole to the total strain, and the double bond 47·2 Kcals/mole. The sum of the two poles for ethylene and cyclopropane is 0·66e, which after correcting for additional strain and reduced capacity (due to bond shortening) is approximately 0·68e. Neglecting capacity differences, the partial pole in each bond is proportional to the square root of the strain component, so the single bonds contribute 0·286e, and the double bond 0·394e. It should be noted that this result is also obtained from similar reasoning to the bicyclobutane case; each single bond is the same as a cyclopropane bond, except that it is under potential from three bonds instead of two, and each bond contributes 1·5 times the cyclopropane pole. The double bond is found by difference—the same reasoning cannot be applied to it, because there are no other analogous bond systems with which the effect of further potential provides a comparison.

The final problem is now geometric. What is needed is the centre of charge for the single bonds and the double bond. It can probably be assumed that the methylene carbon is essentially the same as a cyclopropane methylene, in which case the orbitals will make an angle of $28\frac{1}{2}°$ with the C—C bond line. If it is assumed that this bond is symmetrical, this leads to an electric moment, due to the single bonds, of 0·52D towards the methylene carbon. If it is further assumed that the angle the projection of the double bond in the cyclopropane plane makes with the C—C axis is a quarter that of the corresponding single bond (since half the strain is being absorbed by twice the bonds), then the double bond gives rise to an electric moment of 0·99D. Thus cyclopropene has a calculated electric moment of 0·47D, towards the double bond, compared with an experimental value of 0·455D.[12]

Cyclobutene

If an analysis is applied similar to that of cyclopropene, the 1,2 bond (double bond) has a pole of 0·375e, displaced from the C—C bond line by 0·326 Å, the 3,4 bond has a pole of 0·066e while the other bonds have 0·0855e. Since the Sp^2 carbon has a smaller Van der Waals radius than an Sp^3 carbon, there are probably no non-bonded repulsions, and these will be neglected.

The molecule is best treated as a *cis* disubstituted double bond compound, with back moments due to the poles in the single bonds. To apply equation 5, the C═C—H bond angle must be known, but unfortunately this does not seem to be available. Since this angle is normally 120°, and is approximately 148° in cyclopropene,[12] the angle will be assumed to be 132°. This gives a final moment of 0·19D, which is in reasonable agreement with the experimental value of 0·132D. (A C═C—H angle of approximately 130°54′ gives the experimental value).

Some confirmation of the increase of electron density with strain comes from the measurement of bond lengths. Since the pole charge in the single bonds of 3-membered rings are in the proportions: Cyclopropane (1), cyclopropene (1·5), bridgehead bicyclobutane (2), it might be expected that the bond lengths might reflect this. The experimental values are: Cyclopropane[13] 1·535 Å, cyclopropene[14] 1·515 Å, bridgehead bicyclobutane[15] 1·49 Å. This gives the rather unexpected result that the more strain in the bond, the shorter it is. However, this is expected on the present hypothesis, since progressively more charge over and above that required for a "normal" bond is added with strain.

Thus it can be seen that this hypothesis does relate with reasonable success, work, bond length and electric moments. The electric moment data are in quite good agreement with experiment in most cases—the worst exceptions being the halo acetylenes and vinyl fluoride, and these are cases that might be expected to be most likely to disagree. Of course these effects may only be contributions, since the capacity was quite empirical (although it is, numerically, of reasonable magnitude), but this reasoning from the Hellmann–Feynman Theorem indicates that some such contributions *must* exist, and it seems somewhat unlikely that some other effect is present *exactly proportional* to this in so many compounds. And as will be shown in subsequent papers, good correlations can be obtained with other properties, such as acidities. Thus it is felt that, although it is still extremely difficult if not impossible to arrive at the properties of these systems on purely theoretical grounds, sufficient theory is available to semi-empirically extrapolate properties of easily obtainable strained systems to those not so easily obtained. It is hoped that this series of papers will throw some light on these extrapolation processes.

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