PRESIDENTIAL ADDRESS.

DELIVERED AT THE 113TH ANNIVERSARY MEETING OF THE CHEMICAL SOCIETY AT THE UNIVERSITY, MANCHESTER, ON APRIL 2ND, 1954.

Signs of a New Pathway in Reaction Mechanism and Stereochemistry.

By C. K. INGOLD, D.Sc., F.R.I.C., F.R.S.

LAST year my scientific Address had a somewhat historical tone, and so, to make a change and restore balance, I shall give the present Address a slightly futuristic flavour. Its theme will be that organic chemists interested in the theory of their subject, in the properties of the molecules and in the mechanisms of their reactions, and in how the physical properties bear on the reactions of the molecules, organic chemists, particularly, who would not be content only to fill out the theory of organic chemistry in its present form, but would wish to prepare the ground for a future, more fundamental form, should consider the significance of molecular electronic spectra.

The reason is easily understood. Electron distribution and motion in molecules, as in atoms, is quantised. But because, in general, the stationary states lie energetically far apart, most molecules spend the whole of their lives in one state, the least energised one, which we call the ground, or normal, state. However, all the other states, the so-called excited states, simply by their potential existence, and even if the molecule will never occupy any of them, determine important properties of the normal state, particularly those properties which are of main importance for reactions.

To be specific, the excited states determine that group of properties of the normal state which we summarise in the term " polarisability," using this word, as chemists, in a much more general sense than that which a physicist would seek to express by a coefficient or even a tensor, and including in it the capacity of the system for general and local changes of nuclear and electronic position and motion under every type of deforming force, macrophysical or microchemical.

The nature of excited states determines this " generalised polarisability " of the normal state, because electronic and nuclear position and motion are quantised, and, to this extent, polarisability itself is a quantised property. A deforming force cannot, for example, push the electrons quantally just where it would push them classically. It can only mix with their original distribution and motion a component, depending for magnitude on its intensity, of that particular distribution and motion which belongs to one and/or another of the permitted stationary electronic states. With respect to their control of the polarisability of the occupied normal state, the unoccupied excited states can be pictured as providing certain, sharply defined, more or less steep, openings or roads, into any of which the electrons and nuclei can be partly driven by deforming forces, to an extent depending on the forces, and on how wide the openings are, how steep they are, and in what directions they lie with reference to the forces. (This description has to be broadly interpreted, inasmuch as our metaphorical " roads " provide not only new possible positions, but also new possible motions, for the electrons and nuclei: they are " phase-space " roads.) It should be made clear that a molecule impelled to use these opportunities is still in its normal electronic state, even though, under the deforming forces, that state is modified, having had *dissolved* in it, so to speak, some of the character of one or more of the excited electronic states.

When we reflect that chemical reactions are special consequences of the deformations induced in some molecules by forces due to others, we see at once how important for a physically based theory of chemical reactions must be a knowledge of the excited electronic states of the reacting species.

It is hardly necessary to add that there is much also for the stereochemist, and for the physical chemist, in the study of excited electronic states of molecules. Now that these investigators have discovered so much of what there is to know about the shapes and sizes, and about the mechanical and electrical properties, of most of the simpler typical molecules in their normal states, they should be attracted by the wealth waiting to be won in new knowledge about the morphological and electromechanical properties of excited molecules, new knowledge of a kind whose intrinsic interest, apart from its applications, is their own particular concern.

The excited electronic states of molecules are too highly energised to be thermally accessible. They are photochemically accessible, but are metastable, and with few exceptions, have short lives. We cannot hold a molecule in an excited state, as it holds itself in its normal state, while, taking our time, we carry it round the well-ordered physico-chemical laboratory, determining its geometrical, mechanical, and electrical characteristics by the various standard techniques for which the equipment is there set up. Physical information about an excited state can only be wrung out of the light which is absorbed or emitted when the molecules are springing between that state and some other, usually the normal state. And thus we are led to the study of electronic spectra, which, as you know, occur mostly in the ultra-violet.

I first got led (one might almost have said " kicked ") into using spectroscopic methods through concern, as an organic chemist, with a normal electronic state : for that, the relevant spectra were vibration-rotation spectra. This was in the early 1930's, when the theory of mesomerism was still on trial, and the most typical of mesomeric molecules, benzene, was being stated by spectroscopists, who commanded the most accurate of known techniques for the study of molecular form, to be devoid of mesomeric symmetry. Eventually this difficulty was resolved, with a reversal of that particular conclusion and the production of a somewhat detailed characterisation of the normal state of benzene, by a method which was then new, though it is commonly used today in the study of molecular structure, namely, the *analysis in parallel* of the spectra of isotopic isomers, our benzene isomers being based on the use of deuterium, which was itself a new chemical discovery at that time.

This satisfactory result suggested that the spectral comparison of isotopic isomers might also help with the characterisation of excited molecular states on the basis of electronic spectra. Here was a field in which new effort of some kind was obviously required. Scores of discrete electronic band spectra had been described, but, except for diatomic molecules, none of them had been analysed sufficiently to allow any single molecular excited state to be given a reasonably precise physical description. By 1948, that is comparatively recently, such a treatment of the first case was completed. It was that of the lowest, singlet, excited state of benzene, the state involved in the very well-known near-ultra-violet spectrum of that molecule. This excited state was fairly fully characterised with respect to its dimensions, internal-force system, and electronic type.

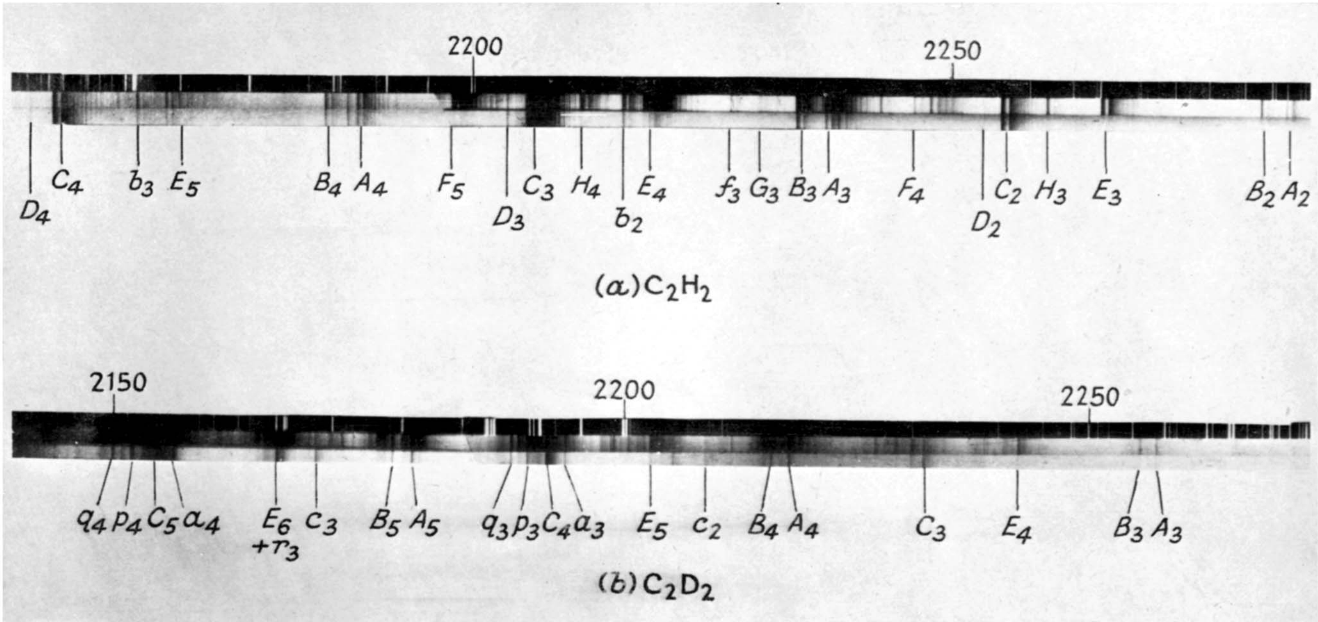
It might seem a little odd that this degree of success in the analysis of a polyatomic electron-spectrum should have been first achieved with a 12-atom molecule, benzene, rather than with some much simpler molecule, such as water or carbon dioxide. But one can suggest a reason. In this lowest, singlet, excited state of benzene, the very stable, aromatic electron-shell is not wholly broken down : it is weakened but preserved, with the result that the excited molecule bears a close general resemblance to the normal molecule, and, in particular, is of exactly the same shape, and very nearly the same size. Such a geometrical similarity of two combining states renders a spectrum simpler and more regular, and very much easier to analyse, than if some drastic reorganisation of the molecular framework had accompanied excitation. But the close similarity also renders this particular excited state much less interesting than some others would be for the interpretation of benzenoid reactions. However, we may reasonably assume that such preservations of basic structure are somewhat exceptional, and that gross changes of structure will often accompany the excitation of valency electrons, which are, after all, the " stanchions " of the structure. I think that one of the reasons why success has come so slowly in the interpretation of polyatomic electron-spectra is that analysis has too often been attempted under the unwarranted preconception that stereochemical form would be approximately preserved. At any rate, it is just when it is not preserved that we have an excited state which could determine a specific kind of polarisability of particular importance for reactions.

To Dr. G. W. King and myself (and the substance of this Address is as much his as mine, though it is only I whom you see) it was clear that the next step in the exploration of lower excited states, as an approach to the interpretation of reactions, should be concerned with a less internally stabilised molecule than benzene. We chose acetylene for its relative simplicity. Its near-ultra-violet absorption spectrum had been described many times, but had never been successfully analysed. Dr. King recorded this spectrum, and the corresponding spectrum of dideuteroacetylene; and he extracted from their combined analysis a fairly complete and accurate account of the excited state, which proved to be widely different in form and constitution from the normal state.

An Address provides an opportunity to explain the principles of such an investigation, without troubling about all the formulæ and numerical particulars that necessarily encumber an original publication. Let us then consider the problem, starting with the experimental observations.

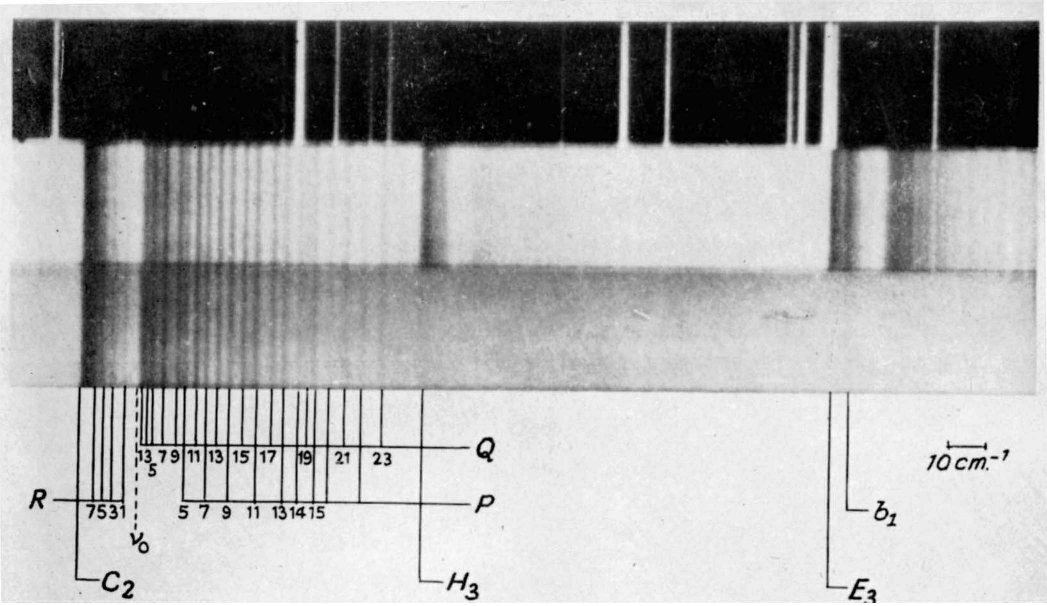
For both the isotopic forms of acetylene, C_2H_2 and C_2D_2, the near ultra-violet band-system, as observed in absorption, starts weakly near 2400 Å, and continues with " ups and downs," but

FIG. 1. *Part of the near-ultra-violet absorption spectrum of acetylene and dideuteroacetylene.*



(Top) *Iron-arc comparison spectrum.*
(Central) *Absorption spectrum with gas at* +20°.
(Bottom) *Absorption spectrum with gas at* −80°.

Fig. 2. *Enlargement of absorption spectrum of acetylene between* 2250 *and* 2270 Å, *showing, in particular, the rotational structure of band* C_2.

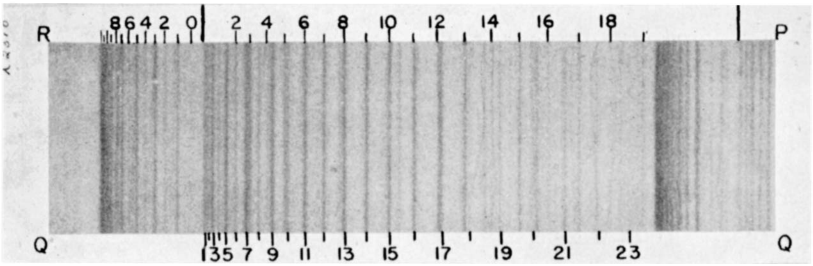


(Top) *Iron-arc comparison spectrum.*

(Central) ***Absorption spectrum with** gas at* +20°.

(Bottom) ***Absorption spectrum with** gas at* −80°.

Fig. 3. *Enlargement of the absorption spectrum of acetylene between* 2310 *and* 2317 Å, *as observed in the fourth order of a* 21-*foot grating, showing, in particular, the rotational structure of band* C_1.



Note the alternation of line intensities, which is due to the spin of the hydrogen nuclei, and the consequent co-existence of ortho- and para-forms of acetylene. This photograph was very kindly presented by Dr. G. Herzberg and Dr. K. K. Innes for illustration of this Address.

generally increasing strength, to 2100 Å, where it becomes overlapped by another band-system belonging mainly to the vacuum-ultra-violet. Up to the point of overlap, the spectrum of either acetylene contains rather less than 100 measurable bands, but without any obvious regularity of arrangement, as will be clear from the segments of spectra, each for two temperatures, shown in Fig. 1. Now the normal acetylene molecule is linear. If the excited state were also linear, we should expect to see, just as for diatomic molecules, a simple repeat-pattern of regularly spaced bands. Here then is a first hint that the upper electronic state is not linear.

Of course, the fact that the spectrum consists of many bands indicates the presence of various numbers of quanta of one or more vibrations in either or both of the combining states. We can distinguish to which electronic states these vibrational quanta belong by a study of the temperature dependence of band intensity. Some bands, for instance those labelled *C*, are not weakened by cooling the gas. Others, such as those labelled *A* and *B*, are weakened moderately. Others, again, such as those termed *E*, are weakened more. Yet others, such as those called *F*, are weakened more still. Two further classes of bands can be observed, which, in successive degrees, are even more temperature-sensitive. The half-dozen of classes into which the bands fall with respect to their temperature-sensitivity distinguish the different vibrational levels of the normal electronic state, from which, in absorption, the transitions start: those levels with more vibrational energy are more strongly depopulated by cooling, with consequent weakening of the bands. This consideration allows us to sort out the vibrations, whose frequencies we shall deduce from the band separations, into those which belong to the normal state, and those which belong to the excited state.

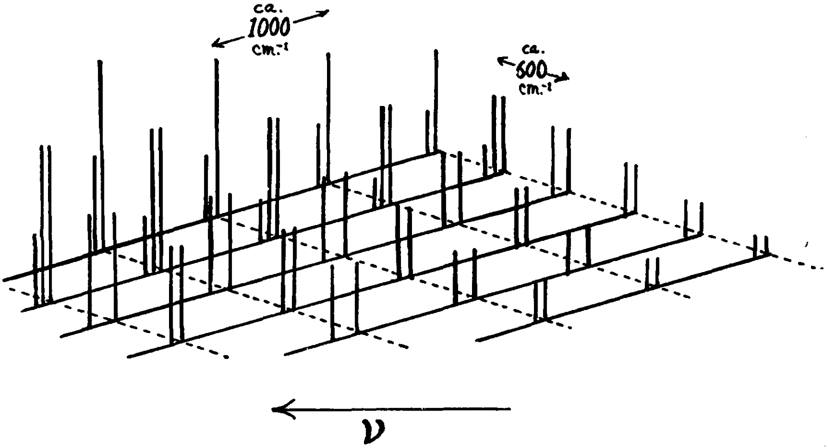
Let us now make a similarly brief, preliminary inspection of the rotational fine structure of the bands. One of Dr. King's enlargements of a band is shown in Fig. 2. At first sight, the pattern looks like one of the two standard patterns, which are given by diatomic molecules, and are expected to be given by all linear molecules, namely, the pattern formed when, in the transition, the electrons oscillate, not along, but across the internuclear line: there is an *R* branch running one way, and overlapping *Q* and *P* branches running the other. Through the kindness of Dr. Herzberg and Dr. Innes, I can show you a much better photograph (Fig. 3), obtained by them with Dr. Herzberg's much larger spectrograph. However, the pattern is not quite as simple as it looks; for when we measure the line positions, and compare them with the standard formulæ for linear molecules, we find that, relatively to the lines of the *P* and *R* branches, which are consistent among themselves, the lines of the *Q* branch are too widely spread; so that for the total band, we have to assume two spacing constants, instead of only one. These spacing constants depend on the large moments of inertia of the molecule; and so we have to conclude that, corresponding to the two large, equal, moments of inertia of linear normal acetylene, there must be two large, but unequal, moments of inertia in excited acetylene, which therefore cannot be linear.

Let us look a second time, and now more closely, at the coarse structure of the spectrum. In seeking to understand such a situation, it is better at first to consider it semiquantitatively, indeed, almost qualitatively, without troubling about precise values: the quantitative fit will come by itself when the right qualitative idea is found. First, we pick out the bands of the temperature-independent class: we find that they form a series of small clusters, roughly 1000 cm.$^{-1}$ apart in C_2H_2, and 800 cm.$^{-1}$ in C_2D_2. Proceeding to the next more temperature-sensitive class, we find that these bands form a similar progression of clusters, again about 1000 cm.$^{-1}$ apart in C_2H_2 and 800 cm.$^{-1}$ in C_2D_2, but shifted bodily to lower frequencies by roughly 600 cm.$^{-1}$ in C_2H_2 and 500 cm.$^{-1}$ in C_2D_2. All these numbers have to be rough, because each band-cluster contains two or three bands, spread over a range of the order of 100 cm.$^{-1}$; and, as the clusters are not all alike, we do not know from what precise point within each cluster to measure the separation of the clusters. The next more temperature-sensitive class is again similar, and shows a similar, further shift by about 600 or 500 cm.$^{-1}$ to lower frequencies; and so on, throughout the remaining temperature classes. Thus, when we take an " aeroplane view," instead of a " ground-level view " of the spectrum, we see (Fig. 4) that the bands do have a pattern. Actually this " two-dimensional pattern," as we may call it, is repeated, more weakly, a second and a third time, with displacements to higher frequencies by other, unrelated intervals, which will be mentioned again later, the three two-dimensional patterns overlapping.

Apart from the complication of having a band-cluster, instead of a single-band, at every point in the two-dimensional pattern, the meaning of this pattern is clear. The interval of about 600 cm.$^{-1}$ in C_2H_2 between successive temperature classes of bands must, as I have explained, be a vibration frequency of the normal state, and the interval of about 1000 cm.$^{-1}$ between successive band-clusters of a temperature class, must be a vibration frequency of the excited state.

Thus the energy diagram is as shown in Fig. 5. We conclude that there is a vibration, of frequency about 600 cm.$^{-1}$ in normal acetylene, and about 1000 cm.$^{-1}$ in excited acetylene, which undergoes *unrestricted quantum changes* during the conversion of one state into the other. Now the Franck–Condon principle teaches that the only vibrations which can appear thus freely in an electronic transition are those which *have inevitably* to be aroused in order to convert the shape of the molecule in one state into its shape in the other. Hence, if we can identify the vibration responsible for the pattern, we shall know how the two shapes differ. This identification is easy: we know from infra-red and Raman spectra the normal-state frequencies of all the five vibrations of acetylene, and of dideuteroacetylene. From the list of them (Fig. 6), we

FIG. 4. *Schematic representation of the " two-dimensional " pattern of bands, which recurs in the first ultra-violet band-system of* C_2H_2 *and of* C_2D_2. *The full-lines join bands whose intensities have the same temperature coefficient. The temperature dependence of band intensity increases along the broken lines towards the " fore-ground." Rotation is responsible for the appearance of a small cluster of bands, instead of one band, at each " lattice point " of the two-dimensional pattern.*



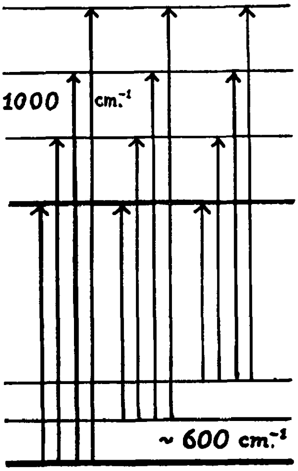


FIG. 5. *Energy diagram corresponding to the two-dimensional pattern of band clusters. The thick horizontal lines represent the energies of the normal and excited electronic states without vibration, whilst the thin horizontal lines indicate the energies of these states when in possession of one, two, etc., quanta of the vibration responsible for the pattern. The vibrational spacing is much magnified, relatively to the electronic spacing. The vibration concerned is the chief of those needed to interconvert the shapes of the two states, a* trans-*bending vibration of the normal state, and a straightening-bending vibration of the excited state. The indicated transitions correspond to the first four band clusters of each of the first three temperature classes.*

see that the only vibration which could conceivably be made responsible for the normal-state frequencies, found in the ultra-violet spectrum, of about 600 cm.$^{-1}$ in C_2H_2 and about 500 cm.$^{-1}$ in C_2D_2, is the *trans*-bending vibration, the fundamental frequencies (that is, the frequencies of the first quantum) of which are actually 613 cm.$^{-1}$ in C_2H_2 and 511 cm.$^{-1}$ in C_2D_2. Therefore the first excited electronic state of acetylene must be a *trans*-bent state.

From this point the way is all down-hill to a quantitative answer. We look a second time, and more closely now, at the rotational fine structure. We bear in mind that the *trans*-bent model shows qualitatively that, because of the relative lightness of hydrogen, there must be one axis of uniquely small inertia (axis *a* in Fig. 7), round which rotation will be singularly rapid, and its quanta singularly large. The rotations about the two axes of large inertia (axes *b* and *c* in Fig. 7) will be slow, and their quanta much smaller. The two orders of magnitude of the rotational quanta will cause the lines of a complete band to separate into several bunches, each of which, though constitutionally only part of the band, will have all the appearance of being itself a band, with its *P*, *Q*, and *R* branches. This is the explanation of what we called the "band clusters." The separations of the bands of a cluster measure the large rotational quanta, while the separations of the lines of the *P* and *R* branches, on the one hand, and of the *Q* branch, on the other, measure the two sorts of small quanta. These values give us the three moments of inertia of the excited molecule, and such data for both C_2H_2 and C_2D_2 permit a quantitative determination of molecular form. The excited molecule is thus found to be accurately planar, *trans*-bent, and centro-symmetrical. The bond lengths and angles are shown in Table 1, where they are compared with the known geometrical data of the normal molecule. We see that the excitation has produced a gross angular change from 180° to 120°, and also a considerable elongation of the C–C bond, as well as some elongation of the two C–H bonds.

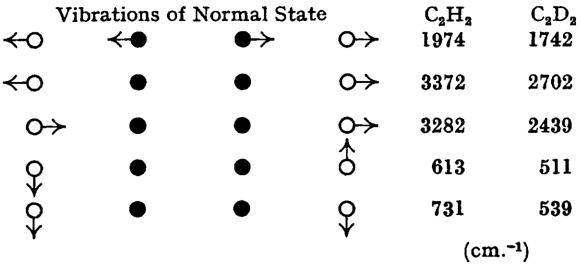


FIG. 6. *Fundamental vibration frequencies of the normal state of acetylene and dideuteroacetylene. The frequencies show that no vibration other than the* trans-*bending vibration (second from bottom) could be responsible for the two-dimensional pattern of bands found in the ultra-violet absorption spectrum.*

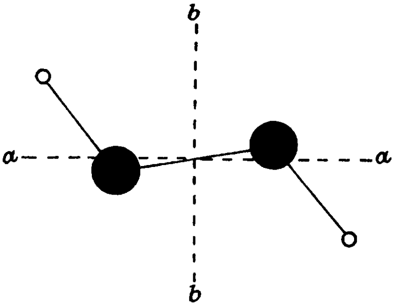


FIG. 7. *Model of metastable* trans-*bent acetylene showing the position of the axes of inertia. Only axes a and b are shown: axis c is perpendicular to both, and thus perpendicular to the plane of the molecule. The moment of inertia about axis a is much smaller than are the moments of inertia about axes b and c, so that the frequencies and quanta of rotation about a are much larger than those about b and c. The co-existence of large and small rotational quanta causes the lines of a complete band to separate into distinct bunches, each of which looks like a band, so that we see a "cluster of bands" where a single band might have been expected. For C_2H_2 the determined values of the moments of inertia are $10^{40}I_a = 2{\cdot}24$, $10^{40}I_b = 24{\cdot}83$, $10^{40}I_c = 27{\cdot}09$ g.-cm.^{2}. That the sum of the first two equals the third (to within the accuracy of their determination) shows that the molecule is planar.*

TABLE 1. *Stereochemical parameters of normal and excited acetylene*

	Normal	Excited
C–C bond length (Å)	1·208	1·385
C–H bond length (Å)	1·058	1·08
CCH bond angle	180·0°	120·2°

Let us now pass from the geometrical to the mechanical characteristics of the excited state. One result of our rotational analysis is that we now know the point within each band cluster from which to measure its separation from other clusters, without including any rotational energy in the measurement of vibrational energy. Measured in this way, the *trans*-bending frequencies of the normal state agree exactly with known values, for instance, with 613 and 511 cm.$^{-1}$ for the first quantum in C_2H_2 and C_2D_2, respectively. Similarly, we can get the exact frequencies of the related bending vibration of the excited state. We have just noticed that in the excitation, the C–C and C–H bonds become elongated; and this means that, in addition to the strong bending motion, a certain amount of the C–C stretching vibration, and a little of the symmetrical C–H stretching vibration, will be needed in order to interconvert the structures.

Now I mentioned that the two-dimensional pattern of bands, which itself is due essentially to the involvement of many quanta of the bending vibration, is more weakly repeated in the spectrum, with displacements by single quanta of two other vibrations of the excited state. These displacements give us the C–C, and the symmetrical C–H stretching frequencies of the excited state; and, knowing them, as well as the bending frequency, for both C_2H_2 and C_2D_2, we can calculate the internal force-system of the excited molecule. The fundamental frequencies of excited C_2H_2 and C_2D_2, thus deduced, are in Table 2. The elastic constants of the excited state, computed in the conventional form of bond-stretching bond-angle-bending force-constants, are in Table 3, where they are compared with the known corresponding constants of the normal state. We see that the bonds are easier to stretch, but much harder to bend, in the excited state than in the normal state.

TABLE 2. *Fundamental frequencies* (*cm.*$^{-1}$) *of excited acetylene and excited dideuteroacetylene.*

	C_2H_2	C_2D_2
C–C stretching	1380	1310
C–H stretching (in phase)	3000	2215
CCH bending (straightening)	1049	844

TABLE 3. *Elastic constants of normal and excited acetylene.*

	Normal	Excited
C–C stretching (dyne/cm.)	$15{\cdot}8 \times 10^5$	$7{\cdot}2 \times 10^5$
C–H stretching (dyne/cm.)	$6{\cdot}0 \times 10^5$	$5{\cdot}1 \times 10^5$
CCH bending (dyne-cm./radian)	$1{\cdot}5 \times 10^{-12}$	$8{\cdot}5 \times 10^{-12}$

Finally, we must determine the electronic structure of the excited state. The fact that its bond angles have been reduced to 120°, shows already that the σ-bonding (or σ-hybridisation) has changed completely from acetylene-type to ethylene- or benzene-type. It follows that, one of the two π-orbitals of the original triple bond must have been broken into two unshared-electron orbitals. These, after they have accommodated the two electrons of the broken orbital, still have two vacant places, and therefore more than enough room for an electron excited out of the remaining π-orbital. That this is indeed the mechanism by which the molecule achieves its energetically lowest electronic excitation is shown by the band forms. Their three-branch character requires that, in the excitation, the electrons oscillate across the line of the nuclei in the normal state, and across the plane of the nuclei in the excited state; and this in turn means that, in the excited state, one electron has been lifted out of the π-orbital, for which the molecular plane is a nodal plane, and has gone into a σ-type of orbital, for which that plane is not a nodal plane. So we arrive at the picture shown in Fig. 8 of the excited molecule, with ethylene-type hybridisation, but with a 3-electron C–C bond, *trans*-hydrogen atoms, and 1½ unshared electrons on each carbon atom in *trans*-positions.

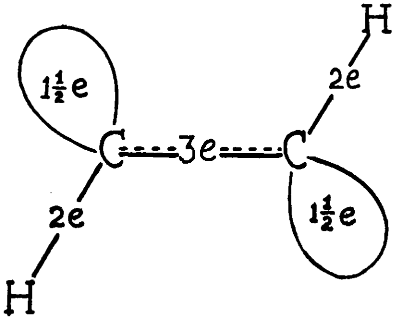


FIG. 8. *Schematic representation of the stereochemistry and electronic structure of the first excited state of acetylene. The stereochemistry is that of ethylene with two* trans-*related hydrogen atoms removed. The* C–C *bond is a three-electron bond of the constitution* $\{(2sp^2)\sigma\}^2\{2p\pi\}$, *as in normal benzene, while the* C–H *bonds are two-electron bonds,* $\{(C2sp^2)(H1s)\sigma\}^2$, *as in either normal ethylene or normal benzene. The remaining valency-shell electrons, assigned to the number* 1·5 *to each carbon atom, are in* $\{2sp^2\}$ *orbitals, and are essentially unshared; but each carbon nucleus has a little concern with the unshared electrons of the other carbon atom, and to this extent " completes its octet."*

This is an excited molecule : the simplest normal molecule, whose C–C and C–H bonds both have electronic constitutions like those of the bonds of excited acetylene, is normal benzene. It is therefore of interest to compare the geometrical and mechanical constants of normal benzene and excited acetylene. As Table 4 shows, these constants are almost the same—indeed most of them are the same to within the accuracy of the figures. Thus the *trans*-bent state of acetylene, except that it is the *trans*- rather than the *cis*-stereoisomer, is quite similar to one-third of the benzene ring. I have little doubt that the spectrum of the *cis*-bent state of acetylene is present among the band-systems which can be seen further out in the ultra-violet. This *cis*-bent state should be very like indeed to one-third of the benzene ring.

I have described the discovery of metastable *trans*-bent acetylene at some length, because it is as yet the only quantitatively characterised state of major interest in this still embryonic line of enquiry into the factors of molecular polarisability, in the chemically generalised sense of that term. Since the *trans*-bent state is the lowest excited state, we may infer that, on the approach of an electrophilic reagent to a normal acetylene molecule, the latter will display a strong tendency to throw up active electrons in *trans*-positions : in terms of our metaphor, this particular "road" is not very steep. And, although much detail remains to be filled in, we may connect this expected tendency with the known general importance of *trans*-additions to acetylenic compounds.

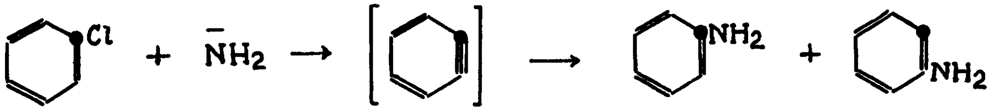
TABLE 4. *Comparison of geometrical and mechanical constants of normal benzene with those of excited acetylene*

	Normal C_6H_6	Excited C_2H_2
Dimensions :		
C–C bond length (Å)	1·39	1·385
C–H bond length (Å)	1·08	1·08
CCH bond angle	120·0°	120·2°
Force constants :		
C–C stretching (dyne/cm.)	$7·6 \times 10^5$	$7·2 \times 10^5$
C–H stretching (dyne/cm.)	$5·1 \times 10^5$	$5·0 \times 10^5$
CCH bending (dyne-cm./radian)	$8·0 \times 10^{-12}$	$8·5 \times 10^{-12}$

On the other hand, the acetylenic bond also must possess a form of polarisability which allows it to produce active *cis*-positions, as we know it does in additions, such as Diels–Alder synthesis, in which *trans*-reaction is sterically precluded. Such polarisability must be controlled by the *cis*-bent excited state; and indeed this consideration is the main reason for postulating the existence of a *cis*-bent metastable form of acetylene.

I suggested that the *cis*-bent state of acetylene should be very like one-third of the benzene ring. Conversely, if we could eliminate two *ortho*-hydrogen atoms from benzene, the residue should be very like the *cis*-bent state of acetylene. This, in essence, is the explanation recently given, with strong experimental support, by Professor J. D. Roberts of certain nucleophilic substitutions in aryl halides, having *ortho*-hydrogen, by amide ions, which, as very strong bases, could be supposed to dehydrohalogenate the aromatic substance and are in fact found to enter partly into the position of the displaced halogen and partly, instead, into the *ortho*-position. He has shown this convincingly for chlorobenzene itself by labelling with ^{14}C, as I have labelled with a spot (Fig. 9), one of what would otherwise become, on this theory, two completely equivalent ring positions, and obtaining, as the theory requires, just 50% of substitution in each of the two positions.

FIG. 9. *Illustrating the proof given by J. D. Roberts and his co-workers that the basic amination of an aryl halide involves a "benzyne" intermediate. The carbon atom marked with a spot was labelled with* ^{14}C, *and it was found that the amino-group went equally into this position and into the* ortho-*position. (The formal triple bond may be regarded as "opened," as it would be in the* cis-*stereo-isomer of* trans-*bent acetylene.)*



The study of the transitions and polarisability of acetylene has only begun : other excited states await discovery; and the relevant polarisability terms must be computed. However, the investigation oultined indicates a path which can probably be followed a long way. In a recent, highly suggestive, theoretical discussion Dr. Walsh has adduced detailed arguments to the effect that gross changes of form and constitution should be the rule, not the exception, in valency-shell excitations. And some evidence of the truth of this can be found in previous incomplete analyses of the spectra of several molecules, besides acetylene, most of them prototypes of large classes of organic molecules. As early as 1938, Dr. Price and Miss Simpson suggested that some of the excited states of carbon disulphide must be bent, and in 1941 Professor Mulliken made the same suggestion for the lowest excited state in particular: the simple point is that the high complexity of its band system would be unaccountable otherwise. I have Dr. Herzberg's permission to mention that he and Dr. Innes have recently found that the first excited state of hydrogen cyanide is bent, and that they are now engaged in a more quantitative evaluation of this state. There is a large literature of the first electronic band-system of formaldehyde; and, though no final analysis has yet been presented, Dr. Walsh pointed out, in the course of the discussion to which I referred, that the two most reasonable outlines of interpretation both involve the conclusion that the excited state is pyramidal. If, to this collection of cases, we add the one completed study, that of acetylene, we obtain an overall picture (Fig. 10), which suggests that the line of investigation illustrated has a future. Indeed, I take these various observations and conclusions to be straws showing the way the wind blows—to be portents of what will one day be a large new field of stereochemistry, that of excited states, and a field which will bear an important part of the foundations of a better theory than we have now, of the steric and electronic mechanism of organic reactions.

FIG. 10. *Survey of the stereochemistry of some excited molecular states (qualitative except for* C_2H_2*), as derived by partial or complete analysis of ultra-violet band-systems:* CS_2 *by W. C. Price and D. M. Simpson* (1938); *and R. S. Mulliken* (1941); HCN *by G. Herzberg and K. K. Innes (personal communication)*; C_2H_2 *by G. W. King and C. K. Ingold* (1952; 1953); H_2CO *by A. D. Walsh* (1953).