164. *The Structure of Polyisoprenes. Part III. Ultra-violet Absorption Spectra.*

By L. Bateman and H. P. Koch.

The quartz ultra-violet absorption spectra of highly purified polyisoprenes correspond closely to those of simple ethylenes having the same degree of alkyl substitution at the double bond. This is also true of geranylamine hydrochloride, which shows no obvious characteristic that can be identified with the structural anomaly revealed by *X*-ray crystal analysis. The extent to which spectral variations are a measure of the electronic properties of groups and molecules of this type is therefore discussed—with the conclusion that for formally saturated substituents the correlation is still obscure. Evidence is presented to show that inductive influence is slight, and that interpretations hitherto advanced on the basis of hyperconjugation are unsound.

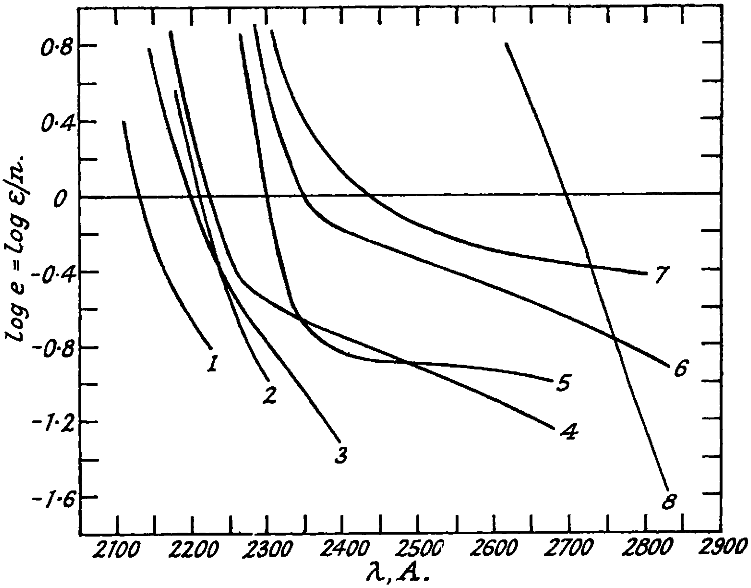
Ultra-violet absorption measurements on polyisoprenes were carried out in 1927 by Scheibe and Pummerer (*Ber.*, **60**, 2163), who compared the optical behaviour of rubber and gutta-percha with that of simple olefins. The considerable advances since made in correlating spectral data with molecular structure and in the theoretical interpretation of the electronic bands, together with experimental progress in the preparation and purification of hydrocarbons, now make a fresh survey desirable. Additional justification is derived from the recent discovery, reported in Part I of this series, that the di-isoprene derivative geranylamine hydrochloride exhibits a new type of hybrid bond character akin to conjugation (Jeffrey, in the press; cf. Bateman and Jeffrey, *Nature*, 1943, **152**, 446).

Isolated olefinic linkages give rise to intense absorption beginning in the neighbourhood of 2000 A. and rising steeply to a maximum near 1850 A., its precise location being governed by second-order environment effects (Carr and Walker, *J. Chem. Physics*, 1936, **4**, 751; Price and Tutte, *Proc. Roy. Soc.*, 1940, *A*, **174**, 207). This characteristic absorption band has been identified by Mulliken (*Rev. Mod. Physics*, 1942, **14**, 265) as an N→V transition from the normal to the first ionic excited state of the double bond. In conjugated systems it occurs at progressively longer wave-lengths, and in general, any change in electronic activation that affects the energy of the N→V transition will be reflected both in a displacement of the actual maximum and in a corresponding shift of the area covered by the absorption band. Since the polyisoprenes do not readily lend themselves to vacuum ultra-violet methods, our measurements were confined to solutions through quartz optics, a technique which fixes a lower wave-length limit of 2000 A. but offers the advantage of accurate intensity data in the accessible region of the steep near-ultra-violet slope of the spectrum.

EXPERIMENTAL.

Spectrographic Technique and Notation.—A small Hilger quartz spectrograph (E 484) was employed in conjunction with the Spekker photometer and a tungsten-steel spark source of ultra-violet light. The spectra were recorded on Kodak B-10 plates, and the match-points determined visually. Except where otherwise stated, pure *cyclo*hexane was used as the solvent in cell lengths of 0·1 to 5·0 cm. Independent determinations carried out on separate samples of the same hydrocarbon provided confirmation that the probable error was less than 3%, which is negligible on the steep portion of the absorption slope.

FIG. 1.



1, 1 : 5-*Hexadiene.*
2, 1-*Pentene.*
3, 1 : 4-*Pentadiene.*
4, cyclo*Hexene.*
5, 2 : 6-*Dimethyl*-2 : 6-*octadiene.*
6, 1-*Methyl*cyclo*hexene.*
7, *Rubber* (*in* C_6H_{12} *containing* 10% EtOH).
8, *Isoprene.*

The molecular extinction coefficient ε is defined by $\varepsilon = (M/lc)\log_{10}I_0/I$, in which $\log_{10}I_0/I$ at the matching wave-length is given directly by the drum-setting of the photometer after allowance for a suitable blank; l is the cell-length in cm., and c the concentration (in g./l.) of the dissolved substance of molecular weight M. The ethylenic extinction coefficient $e = \varepsilon/n$ is also employed in the study of the polyisoprenes and other compounds containing n double bonds in order to obtain comparable intensity values representing the absorption of one ethylenic linkage. With this convention the absorption of rubber is plotted per single isoprene residue, but that of isoprene itself as the absorption of the half-molecule.

Preparation and Purification of Materials.—1-tert.-*Butyl*cyclo*hexene* is the only new compound to be described, but details are also given of the purification procedures adopted for those hydrocarbons whose low-intensity absorption bands are plotted in Fig. 1. The preparative methods employed for the remaining materials not specially purified for low-intensity investigation are briefly summarised at the end of this section.

1-tert.-*Butyl*cyclo*hexene.*—The reaction of *tert.*-butylmagnesium chloride with *cyclo*hexanone produced much undesired *cyclo*hexanol (b. p. 61°/13 mm.) and a poor yield of 1-tert.-*butyl*cyclo*hexanol* (b. p. 80°/13 mm.), which were separated in a Dufton column. This carbinol solidified almost immediately in the receiver (m. p. 49—50°) but was too soluble in the usual solvents to permit of recrystallisation (Found : C, 76·8; H, 12·9. $C_{10}H_{20}O$ requires C, 76·95; H, 12·8%). Distillation of this from a few crystals of iodine readily gave 1-*tert*.-butyl*cyclo*hexene (b. p. 158°/765 mm.), which was kept over molten sodium for one hour and finally redistilled at 51°/14 mm.; $n_D^{19·5°}$ 1·4632 (Found: C, 86·8; H, 13·2. $C_{10}H_{18}$ requires C, 87·0; H, 13·0%).

Spectrographically Pure Hydrocarbons.—Except where otherwise stated, each specimen was distilled through all-glass, grease-free, fractionation apparatus of the Fenske–Whitmore type immediately before optical examination.

1-Pentene and 1 : 4-pentadiene were generated from their pure bromo-ethers which had been obtained by the method of Boord *et al.* (*J. Amer. Chem. Soc.*, 1930, **52**, 3396; 1931, **53**, 1505) as modified by Kistiakowsky *et al.* (*ibid.*, 1936, **58**, 146). The hydrocarbon spectra underwent no further change after three azeotropic distillations with methyl alcohol (b. p. $26·6_5$° and $23·5_0$°, respectively), and the pure olefins boiling at $30·1_5$° and $25·8_0$° were isolated by repeated washings with ice-water.

The low-intensity absorption of 1 : 5-hexadiene, prepared from allyl bromide and magnesium, remained constant after three fractionations at 59·1°. Isoprene was similarly purified (b. p. 33·87°/758 mm.) from the crude hydrocarbon obtained on alkaline distillation of its recrystallised sulphone (m. p. 63·5°).

None of the *cyclo*hexenes could be freed from traces of conjugated dienes by fractionation alone, but both *cyclo*hexene and 1-methyl*cyclo*hexene were produced spectrographically pure on treatment with maleic anhydride (Stücklen, Thayer, and Willis, *ibid.*, 1940, **62**, 1717).

" Dihydromyrcene " (Semmler and Mayer, *Ber.*, 1911, **44**, 2010) has been employed in chemical work as a representative of the di-isoprenic 2 : 6-dimethyl-2 : 6-octadiene hydrocarbon (Farmer and Sutton, J., 1942, 139; Bloomfield, this vol., p. 114), but Dupont and Desreux (*Bull. Soc. chim.*, 1937, **4**, 422) obtained Raman spectra evidence that the reduction of β-myrcene invariably results in a certain amount of 1 : 2- as well as 1 : 4-addition of hydrogen. Apart from this objectionable complication, the spectra of our dihydromyrcene samples also exhibited the typical aromatic band system of *p*-cymene (cf. Bradley and Richardson, *Ind. Eng. Chem.*, 1940, **32**, 963), an impurity which could not be removed by fractionation. 2 : 6-Dimethyl-2 : 6-octadiene was therefore made by the reduction of purified geraniol with sodium in liquid ammonia (Chablay, *Ann. Chim.*, 1917, **8**, 145; Dupont, Dulou, and Desreux, *Bull. Soc. chim.*, 1939, **6**, 83), and we are indebted to Dr. F. Hilton for this preparation. On careful fractionation, the pure hydrocarbon distilled at 61·2°/16 mm.; $n_D^{19·5°}$ 1·4498.

Rubber hydrocarbon was purified down to constant low-intensity absorption by a special precipitation method of fractionation, details of which will be given elsewhere. The final specimen contained N, 0·01% and had a viscosity molecular weight of 330 × 10^3.

Preparation of Other Materials.—1 : 2-Dimethyl*cyclo*hexene was obtained by condensation of methylmagnesium iodide with 2-methyl*cyclo*hexanone and dehydration of the tertiary carbinol product with iodine. After purification *via* the crystalline dibromide (m. p. 142°), the hydrocarbon had b. p. 135°, $n_D^{21°}$ 1·4591.

Geranylamine hydrochloride (Sutton, this vol., p. 306) was crystallised four times from acetone (m. p. 146°) and dried in a vacuum. Oxidation impurities were removed from squalene hydrocarbon by adsorption on a column of alumina. Pure white Tjipetir gutta-percha, obtained by courtesy of the Research Department of the Telegraph Construction and Maintenance Co., Ltd., had N, 0·01%, and a viscosity molecular weight of 78 × 10^3.

DISCUSSION.

Low-intensity Long-wave Absorption of Olefins.—It was noted by Carr and Walker (*loc. cit.*) that even highly purified specimens of hydrocarbons containing isolated ethylenic linkages regularly showed characteristic long-wave absorption tails in addition to the intense N→V bands occurring at shorter wave-lengths. We have confirmed the presence of this weak absorption region in 1-pentene and in *cyclo*hexene (Stücklen, Thayer, and Willis, *loc. cit.*), and we also observed its existence in spectrographically pure preparations of 1 : 5-hexadiene, 1 : 4-pentadiene, 1-methyl*cyclo*hexene, 2 : 6-dimethyl-2 : 6-octadiene, and rubber (Fig. 1). The electronic process responsible for the long-wave ethylenic band has not yet been identified, but is of real significance as it must evidently play an important rôle in the photochemistry of these substances under sunlight conditions. Carr and Walker have already directed attention to the marked increase of this absorption region associated with alkyl substitution of the double bond, and it can be seen from the figure that both methyl*cyclo*hexene and rubber actually absorb more strongly than the conjugated isoprene at wave-lengths longer than 2750 A.

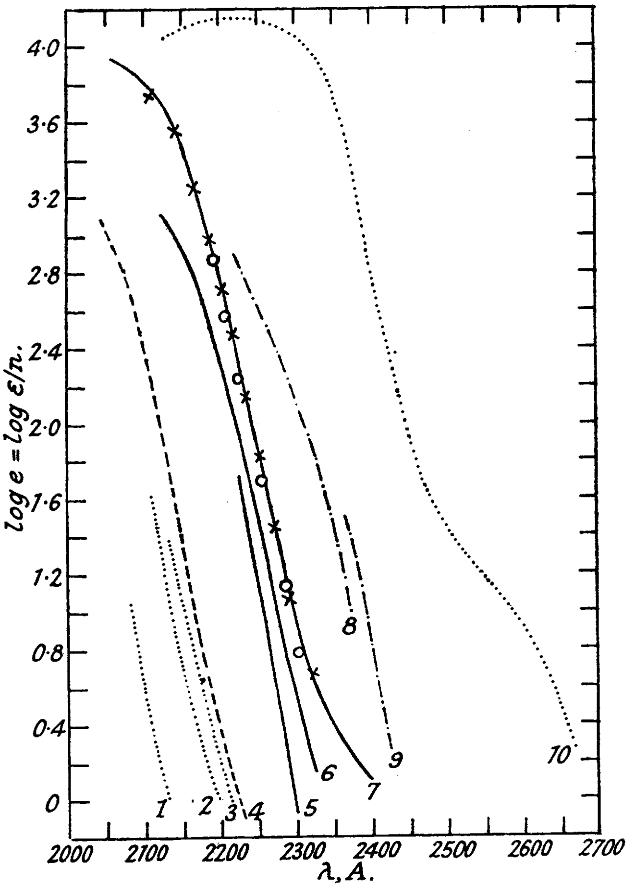
Most of the olefinic spectra reported from Carr's laboratory also displayed inflexions or step-outs of varying intensity in the region of 2300 A. We encountered similar features in our own hydrocarbon specimens before systematic fractionation which revealed that this type of band is caused by minute traces of intensely absorbing contaminants of a conjugated diene structure. Such irregularities are therefore not to be regarded as characteristic of pure olefin spectra, as was indeed suspected by the American authors.

Classification of Intense Polyisoprene Absorption.—The extreme quartz ultra-violet spectrum of the polyisoprenes is compared with that of some related olefins in Fig. 2. The complete coincidence of the absorption curves of rubber and gutta-percha is of interest in view of the geometrical isomerism which is believed to distinguish these two hydrocarbons. Ramart-Lucas (Grignard, " Traite de Chimie Organique," 1936, II, 59) has, however, already refuted earlier assertions that there existed a systematic difference between the ultra-violet spectra of *cis–trans*-isomeric absorbing groups, and the high-intensity N→V absorption of the two forms of 2-butene appears to occur at the same wave-lengths (Carr and Stücklen, *J. Chem. Physics*, 1936, **4**, 760). Most of the existing spectrographic data on pairs of geometrical isomers relate to more complex chromophores than the simple alkyl-substituted ethylenic linkage, and the reduced absorption usually displayed by the *cis*-isomerides can be attributed to their shortened spatial extension or to steric interference between *cis*-ethylenic substituents (Koch, *Chem. and Ind.*, 1942, **61**, 273). The polyisoprene curve also covers our measurements on squalene and is identical with the earlier data on rubber and gutta-percha obtained by Scheibe and Pummerer (*loc. cit.*), whose curve for diallyl is likewise confirmed.

The figure shows that the spectra of the polyisoprenes and other unsaturated hydrocarbons of the tri-substituted type $CR_1R_2{:}CHR_3$ form a well-defined group, clearly differentiated from all other ethylenic compounds, which are either more or less absorptive in accordance with the extent of substitution on the double bond. The precise nature of the alkyl substituents appears to be largely immaterial in this classification provided that no conjugation occurs when more than one double bond is present in the molecule (cf. spectrum of isoprene). Carr and Walker (*loc. cit.*) and Price and Tutte (*loc. cit.*) previously observed corresponding red shifts in the vapour spectra of some simple ethylenes in the vacuum ultra-violet. Analogous long-wave alkylation displacements are also known to occur in the spectra of the conjugated dienes (Price and Walsh, *Proc. Roy. Soc.*, 1940, *A*, **174**, 220; Booker, Evans, and Gillam, J., 1940, 1453) and of olefinic centres conjugated with a carbonyl group (Woodward, *J. Amer. Chem. Soc.*, **1941**, **63**, 1123).

Although the absorption of 1 : 5-hexadiene at the extreme short-wave end of the quartz ultra-violet is in line with this classification, yet the spectra of the monosubstituted ethylenes 1-pentene and 1 : 4-pentadiene appear to lie remarkably close to the curve of *cyclo*hexene, which is more highly substituted on the double bond.

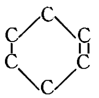
Fig. 2.



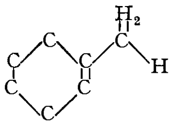
1, 1 : 5-*Hexadiene.*
2, 1 : 4-*Pentadiene.*
3, 1-*Pentene.*
4, cyclo*Hexene.*
5, 2 : 6-*Dimethyl*-2 : 6-*octadiene.*
6, 1-*Methyl*cyclo*hexene.*
7, *Rubber* (*in* C_6H_{12} *containing* 10% EtOH).
× × ×, *Gutta-percha.*
○○○, *Squalene.*
8, 1 : 2-*Dimethyl*cyclo*hexene.*
9, *Tetramethylethylene* (*after Carr and Walker*).
10, *Isoprene.*

According to Carr and Walker, who record different absorption values for 1-pentene, *iso*propylethylene is even more absorptive than *cyclo*hexene in this region. Since the peak of the *iso*propylethylene band is reported to fit normally into its group position (Carr and Stücklen, *loc. cit.*), it seems possible that the irregular spreading-out of the monosubstituted ethylene absorption curves may be due to a peculiar broadening or intensification of the band rather than a genuine wave-length shift.

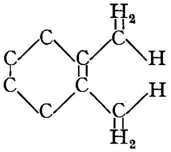
Alkyl Shifts and Hyperconjugation.—Mulliken (*J. Chem. Physics*, 1939, **7**, **339**) developed the theory of hyperconjugation to account for the abnormal long-wave absorption of cyclic conjugated dienes, and used it subsequently to explain the successive absorption shifts effected by alkyl substitution in simple ethylenes. The theory has been generalised and expressed quasi-quantitatively in quantum-mechanical terms, although some of the original views have been drastically revised (Mulliken, Rieke, and Brown, *J. Amer. Chem. Soc.*, **1941**, **63**, 41). Hyperconjugation, which is now considered to find expression in the properties of the ground state rather than those of excited states, is still regarded as determining the red shifts, although decreases in ionisation potential are mainly attributed to charge transfer (Mulliken, *Rev. Mod. Physics*, *loc. cit.*). Since the conjugative powers of saturated bond electrons with unsaturated centres is much greater for C–H than for C–C bonds, the long-wave displacements in the *cyclo*hexene series are due, on this view, to the increasing conjugation inherent in structures (I)—(III). We have been able to test this theory experimentally by examining



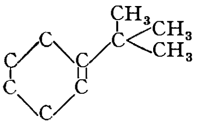
(I.)



(II.)



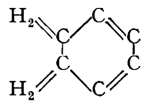
(III.)



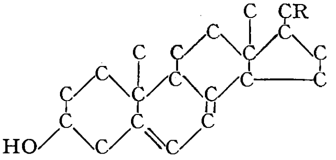
(IV.)

1-*tert.*-butyl*cyclo*hexene (as IV) in which all the side-chain hydrogen atoms necessary for hyperconjugation have been replaced by carbon. The spectrum of this new olefin is given in Fig. 3, and comparison with methyl*cyclo*hexene and other *cyclo*hexenes proves that alkyl shifts are predominantly a function of carbon substitution as such, irrespective of the presence or otherwise of C–H bonds in the substituent group. This result is comparable with Conant and Kistiakowsky's heat of hydrogenation data (*Chem. Rev.*, 1937, **20**, 181) in which negligible differences between methyl-, ethyl-, *iso*propyl-, and *tert.*-butyl-ethylene were found.

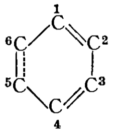
Differing from Mulliken, Price and Tutte (*loc. cit.*) regard alkyl displacements as chiefly due to a reduction in ionisation potential of the ethylenic centre by charge transfer from the adjacent alkyl groups, a process which should lead to parallel changes in heats of hydrogenation. In conjugated *cyclo*hexadiene the $N \rightarrow V_1$ transition occurring at much longer wave-lengths than in the open-chain dienes is similarly related to an alteration in the ground state. If this is correct, it seems remarkable that its heat of hydrogenation does not differ appreciably from that of an analogous butadiene (Conant and Kistiakowsky, *loc. cit.*). Mulliken's alternative explanation of the *cyclo*hexadiene spectrum is open to more serious objection from arguments based on chemical constitution. If hyperconjugation depicted in structure (V) is regarded as determining the red shift from the normal conjugated diene spectrum, then it is difficult to see why substituted *cyclo*hexadienes of the type of ergosterol (VI) should absorb at even longer wave-lengths. In point of fact, all the spectrographic data on polycyclic dienes that have accumulated in recent years (Booker, Evans, and Gillam, *loc. cit.*) serve to show that the incorporation of the conjugated diene system in one six-membered ring is the exclusive cause of the abnormal spectrum regardless of all second-order substitutional influences.



(V.)



(VI.)



(VII.)

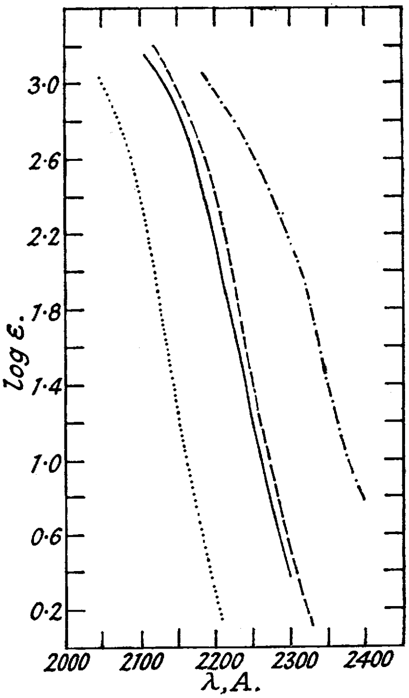
It has been shown beyond doubt that hyperconjugation is an important mechanism of electronic activation in chemical processes (Hughes and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 657), and physical measurements have indicated its influences in the ground state (Hannay and Smyth, *J. Amer. Chem. Soc.*, 1943, **65**, 1931; Baker and Hemming, J., 1942, 191), but it is evident that the spectral features of hyperconjugation have yet to be correctly described.

Interaction of Double Bonds in the Polyisoprene Chain.—There is a generally accepted working hypothesis in ultra-violet spectroscopy that two chromophores contained in the same molecule behave as separate absorbing entities provided they are separated by one or more carbon atoms (Ramart-Lucas, *loc. cit.*). This is borne out by our data on 1 : 4-pentadiene, 1 : 5-hexadiene, and the polyisoprenes, all of which fall into their normal group classification in accordance with the degree of alkyl substitution of the double bond. The spectrographic rule is paralleled by the available thermal data, since the heat of hydrogenation of 1 : 5-hexadiene is almost identical with twice that of a singly substituted ethylene, and the same is very nearly true of 1 : 4-pentadiene (Kistiakowsky *et al.*, *loc. cit.*). The only exception that might be quoted against this generalisation is the spectral anomaly of the cyclic conjugated dienes. Although Price and Walsh (*Proc. Roy. Soc.*, 1941, *A*, **179**, 201) tentatively postulated electronic repulsion between the two *cis*-linked double bonds, or, alternatively, the existence of Dewar type resonance structures in 1 : 3-*cyclo*hexadiene, yet Woodward (*J. Amer. Chem. Soc.*, 1942, **64**, 72) envisaged an incompletely insulating 5 : 6 single bond in a benzene-analogous structure (VII). This formulation would account for the long-wave absorption, but the normal heat of hydrogenation remains a difficulty.

Recent physical evidence points to incomplete insulation of the 1 : 5-spaced double bonds in the polyisoprene chain, comparable with that represented in structure (VII). *X*-Ray analysis of the di-isoprene derivative geranylamine hydrochloride, $CMe_2{:}CH{\cdot}CH_2\overset{\cdots}{-}CH_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}NH_2,HCl$ (Jeffrey, *loc. cit.*), has revealed a significant shortening of the central single bond accompanied by a planar arrangement of the adjacent groups. It has been suggested (Bateman and Jeffrey, *loc. cit.*) that this unique bond character, which simulates normal conjugation, is the result of hyperconjugation. The ethylenic centres are considered to promote hybridisation which partially localises the C–H bond electrons of the central CH_2 groups in the hybrid bond. It is perhaps surprising therefore that the N->V band of the polyisoprenes does not reflect this structural modification and that the spectrographic insulation rule still holds. There is no difference in this respect between di-isoprene itself and its amine hydrochloride, whose spectra are plotted side by side in Fig. 4. Since saturated amine hydrochloride groups are completely transparent in the quartz ultra-violet, the absorption of geranylamine hydrochloride in this region is determined exclusively by the di-isoprene system, and the close coincidence of the two spectra is very striking.

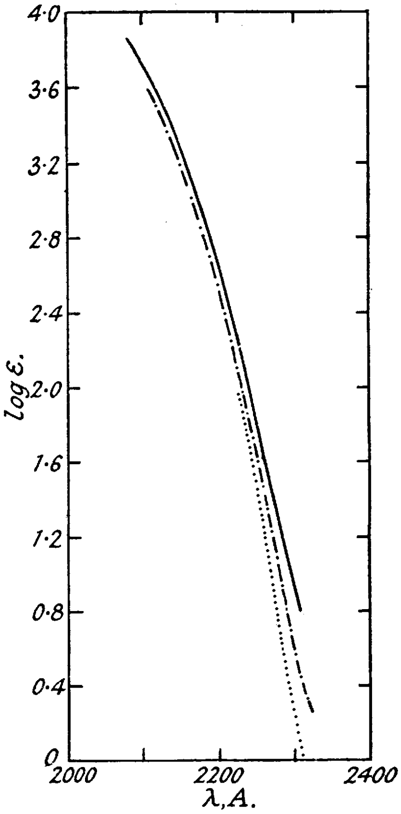
The latter observation is of further interest owing to its bearing on the inductive dependence of N->V transitions (cf. Jones, *Chem. Rev.*, 1943, **32**, 14). Price and his colleagues conclude that the determinative function of alkyl substituents at ethylenic centres is one of charge transfer, which they identify with the inductive mechanism well recognised chemically. Now, it is well known that a substantial fraction of the electrostatic force of an ionic pole is transmitted through one saturated carbon atom. Hence at the nearer double bond in geranylamine hydrochloride there will be an added inductive influence of marked strength directively the same as that of the methyl substituent. Moreover, it is not possible in this case to invoke an alternative and compensating mode of polarisation as in *cis*-dichloroethylene and chloroprene, where correlation between spectral displacement and the inductive power of the chlorine atom was also absent (Price and Walsh, 1940, *loc. cit.*), and we must conclude that double bond absorption is far less sensitive to inductive influence than hitherto believed.

FIG. 3.



·············· cyclo*Hexene.*
—————— 1-tert.-*Butyl*cyclo*hexene.*
— — — — 1-*Methyl*cyclo*hexene.*
—·—·—· 1 : 2-*Dimethyl*cyclo*hexene.*

FIG. 4.



—————— *Geranylamine hydrochloride* (*di-isoprene amine hydrochloride*) *in* EtOH.
—·—·—· 2 : 6-*Dimethyl*-2 : 6-*octadiene* (*di-isoprene*) *in* EtOH.
·············· 2 : 6-*Dimethyl*-2 : 6-*octadiene* (*di-isoprene*) *in* C_6H_{12}.

There appear to be three possible explanations why the spectrum of geranylamine hydrochloride shows no departure from that typical of a substituted ethylene in spite of the unusual character of the central single bond. First, the abnormal bond may be peculiar to the crystalline state; secondly, the presence of the ethylenic centres may not in fact govern the new hybridisation. We see no reason for accepting the former, and regard the latter as improbable. Thirdly, both normal and excited states of the double bond may participate equally in the hyperconjugation process, in the same way, presumably, as they are similarly responsive to the polar force of the ammonium group. However, this problem of the unchanged transition energy must remain unsolved until the true spectral consequence of hyperconjugation is elucidated, and the nature of the unusual hybridisation more fully understood.

Our thanks are due to Dr. D. A. Sutton for supplying samples of dimethyl*cyclo*hexene and squalene for this investigation, which forms part of the programme of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

48, TEWIN ROAD, WELWYN GARDEN CITY, HERTS. [*Received, July 6th,* 1944.]