

their normal positions by the presence of a chemisorbed oxygen monolayer. The effect of oxygen adsorption on the photoelectric sensitivity of bismuth films was discussed by R. Suhrmann (Hannover).

An interesting group of papers on silicon was submitted from the British Associated Electrical Industries group of companies. R. C. Newman and J. Wakefield (A.E.I. Laboratory, Aldermaston) pointed out the possibility of a connexion between the formation on silicon surfaces of etch pits on one hand and of silicon carbide on the other. The distribution of impurities in pulled silicon crystals was discussed, among other topics, in two papers (N. R. Howard; P. Ransom, British Thomson-Houston Co., Rugby). H. F. Mataré (Sylvania Electric Products, Inc., Bayside, N.Y.) reported electrical experiments on bicrystals having known angles of misfit, and drew conclusions about the overlap of wave-functions of dangling bonds which occur at grain boundaries. Further information about these effects was expected at the meeting being held at Rochester, New York, at which a session is being devoted to grain boundaries and dislocations. An interesting aspect of crystal imperfections is their effect on mechanical damping. In silicon and germanium single crystals the damping usually shows two peaks when regarded as a function of temperature. The low-temperature peak at about two-thirds the melting point may perhaps be associated with the movement of dislocations. The high-temperature

peak is probably connected with the motion of dissolved oxygen. A paper on these effects was read by P. D. Southgate (Mullard Laboratories, Salford).

Because of their applications to thermoelectric refrigeration a session was devoted to tellurides. The theory of remanent magnetization, important in connexion with magnetic recording tapes, was discussed by E. P. Wohlfarth (Imperial College of Science and Technology, London). Other applications which were considered included the use of impact ionization of impurities for low-temperature computing elements, applications of fluorescence to post office sorting problems, and several papers on transistor technology. As in the case of the earlier meeting at Garmisch, band calculations were discussed only incidentally. Impurity band conduction was mentioned somewhat more prominently—for example, in some speculations about the transition to metallic impurity band conductivity. The apparent absence of impurity band conduction down to 2° K. in some specimens of InSb was pointed out by E. H. Putley (Royal Radar Establishment, Malvern).

Other stimulating contributions, for example, in magneto-optics, are not mentioned here, since they are included in other conferences this summer. The proceedings of the Brussels meeting have been promised for the end of this year. Those of the 1956 Garmisch meeting are still expected.

P. T. LANDSBERG

## STERIC EFFECTS IN CONJUGATED SYSTEMS

THE consequences of steric interactions in organic molecules are of wide practical and theoretical interest to chemists, but the entire field of steric effects in organic chemistry is too vast to be covered in one conference. "Steric Effects in Conjugated Systems" was therefore chosen as the title for the Chemical Society symposium, held in Hull during July 15–17, because this topic is still of wide appeal to chemists and yet is sufficiently specialized to be treated in considerable detail by some fifteen papers, dealing with the study of steric effects by spectroscopic, kinetic, and other physical methods.

The introductory paper was read by Prof. E. E. Turner (Bedford College, London). He traced the chemical developments which led away from the Kaufer formula for diphenyl to the concept of a molecule comprised of two collinear benzene nuclei which will tend to be planar. This structure allowed an explanation of the optical isomerism of suitable diphenyls carrying four, three, two, or even one substituent in the sterically sensitive *ortho*-positions. This marked the discovery of molecular dissymmetry arising from restricted rotation about a bond—one of the most important steric effects which may arise in a conjugated system—and led to more recent work on 2:2'-bridged diphenyls. The conformational stabilities and molecular configurations for compounds containing two or more atoms in the bridge are now being studied by ultra-violet absorption spectroscopy.

Steric effects in diphenyl were also treated by Dr. G. H. Beaven (National Institute for Medical Research), who discussed the ultra-violet absorption spectra of pure alkyldiphenyls. While a 4-methyl

substituent gives a red shift and an intensity increase of the conjugation band, 2-methyl substitution gives a blue shift and an intensity decrease. Further methyl substitution in the *ortho*-positions increases this effect, and the results are consistent with the hypothesis that progressive introduction of methyl groups into these positions gives progressive deviation from coplanarity and decrease in conjugation. Higher alkyl groups, unless branched, do not increase the steric effect, and the spectrum of 2:2'-dimethyldiphenyl suggests that the molecule has the *cis*-configuration already reported for 2:2'-dihalogenodiphenyls. The vapour-phase chromatography of these alkyldiphenyls was discussed by Dr. E. A. Johnson (National Institute for Medical Research), who has shown that the retention volumes for a single stationary phase depend on the position of the alkyl groups. Thus, 2-alkyldiphenyls have smaller retention volumes than the 3- or 4-isomers, presumably because the lower conjugation in the 2-isomer gives rise to less interaction with the stationary phase. The results confirm the conclusions reached from ultra-violet spectra relating conjugation to position and number of alkyl groups, and it has been possible to identify the peaks of a gas-liquid chromatogram of 21 isomeric tetramethyldiphenyls. Conjugation in 2:2'-bridged diphenyls and in halogenodiphenyls was also discussed in the light of the relative retention volumes for the compounds.

The influence of steric interactions upon the mesomorphic behaviour of 4-*p-n*-alkoxybenzylideneamino-diphenyls and 4:4'-di-(*p-n*-alkoxybenzylideneamino) diphenyls was discussed by Dr. G. W. Gray (University of Hull). A 2- or 2'-substituent in the diphenyl

nucleus decreases the mesomorphic thermal stability more than a 3- or 3'-substituent. Clearly, twisting about the 1:1'-bond interferes with the molecular packing in the mesophases, and indeed increasing size of halogen increases the effect. A methyl group appears to have about the same steric effect as a chlorine, and 2:2'-disubstituted derivatives appear to adopt a *cis*-configuration. It is difficult to assess the configuration of the unsubstituted diphenyl ring system in the mesophases, but the results suggest that it may be planar.

Prof. C. A. Coulson (University of Oxford) described the use of molecular-orbital theory to explain the observed blue wave-length shifts in the ultra-violet spectra of diphenyls when the molecule is twisted about the 1:1'-bond. Reference was made to an alternative procedure developed by Longuet-Higgins and Murrell for such a system *A-B* (*A* and *B* may be groups such as phenyl, nitro-, etc.), and this was thought to be of promise for dealing with nitro-anilines, where a full self-consistent-field molecular-orbital calculation would be complex. Relief of steric strain by displacement was then discussed by reference to the idealized case of a benzene ring folded through an angle about the 1:4-axis. The method of using mean resonance integrals was applied to this condition, which is similar to that occurring in the *paracyclophane* series, and used to explain the observed bathochromic shifts in these compounds. The same method was used to deal with 3:4-benzophenanthrene which on 5- and 4'-methylation gives a progressive red shift which must be due to steric strain. The calculated effective resonance integrals for the mono- and di-methyl compounds agree excellently with those derived from spectra, and, moreover, the observed methyl affinities and the calculated free valences of the hydrocarbon agree well. The technique of using an average resonance integral is safest for such large polynuclear molecules where the strain is uniformly distributed throughout the molecule.

The contribution of Prof. M. J. S. Dewar (Queen Mary College, London) on the light absorption of cyanine dyes also concerned the direction of wave-length displacements arising from deviations from coplanarity. Hypsochromic displacements occur in the unsymmetrical cyanines, but the more unusual bathochromic shifts are observed in symmetrical cases. Prof. Dewar criticized explanations of these effects based on resonance theory, and applied molecular-orbital theory to the problem. While the strain of small distortions may be taken up by twisting about the central bonds in the dye, it is possible that large strains cause distortion of the whole molecule—buckling of rings—and this would lead to bathochromic shifts. Prof. Dewar considered that a more detailed treatment of this kind would be useful.

Steric effects in dyes again featured in the paper by Dr. C. C. Barker (University of Hull) on basic di- and tri-phenylmethane dyes. When the three main types of basic dye—Michler's hydrol blue, malachite green and crystal violet—are substituted, the molecular conformation and the electronic absorption spectra are usually modified, and Dr. Barker related the direction and extent of observed wave-length shifts to the steric and conjugative effects of the substituents. Alkyl derivatives of the three main types were fully discussed, and with malachite green the effects of numerous substituents in the phenyl ring were determined for comparison

with the effects of substitution in the dimethyl-aminophenyl rings.

To the two classes of steric effect in ultra-violet absorption spectra proposed by Braude—steric interactions causing changes in (1) intensity only and (2) both wave-length and intensity—Prof. W. F. Forbes (Memorial University of Newfoundland) adds a third, covering steric interactions which so inhibit conjugation that the system absorbs as two entities. The mechanisms underlying the different types were discussed, although, in the absence of planar reference compounds, the identification of the type of effect may be difficult. Prof. Forbes illustrated the effect of both substituent size and nature of solvent upon the type of steric effect, and mentioned developments to which adoption of the classification may lead.

Dr. E. S. Waight (Imperial College of Science and Technology, London) concluded from measurements of the ultra-violet absorption spectra of conjugated carbonyl compounds at 20° and -196° that type I steric effects cannot be associated with transitions from non-planar ground-states to near planar excited states. From the infra-red and ultra-violet spectra of  $\alpha\beta$ -unsaturated carbonyl compounds, it is concluded that 2-methyl-1-acetylcyclohexane has an *s-cis*-structure, which is not planar. Using the ideas of Longuet-Higgins and Murrell on electronic transitions in the system  $C=C=O$ , it is thought that steric hindrance to planarity will produce Braude's type I effect when the transition is to an electron transfer state, and to a type II effect when the transition involves locally excited states.

Steric effects in monomethyl 1:2-benzanthracenes were discussed by Dr. G. Dallinga (Shell Laboratories, Amsterdam). The basicity constants and rates of H-D exchange for the twelve methyl isomers correspond strictly, but the observed basicities can be discussed in terms of the methyl group's inductive effect only when steric effects do not operate. Steric effects must therefore influence both the basicities and the rates of exchange for these isomers, and it is proposed that the structure for the transition state for the exchange resembles that of the conjugate acid. To explain the enhanced basicity of the 9-carbon atom, a steric repulsion is proposed between the hydrogens on the 9- and 1'-carbon atoms.

The influence of *ortho*-substituents upon the reactivities of groups in aromatic molecules has been extensively studied, since the Hammett equation is useful only in correlating reactivities in *meta*- or *para*-substituted systems, where there is no steric effect. Mr. A. C. Farthing and Mr. B. Nam (Imperial Chemical Industries, Ltd.) have derived a four-parameter, modified Hammett equation for *ortho*-substituted systems:

$$\Delta \log K = \sigma_S \rho_S + \sigma_E \rho_E$$

A graphical test ( $\Delta \log K/\sigma_S$  against  $\sigma_E/\sigma_S$ ) for forty-five reactions in the literature gives a correlation which is good enough to warrant statistical analysis and which suggests that the equation has some empirical validity.

In electrophilic aromatic substitution or side-chain reactions involving an electron-deficient centre, strong resonance interactions occur between the centre and the substituent. Such interactions are unimportant in the ionization of benzoic acids from which Hammett substituent constants are derived, and the constants cannot be used to treat the above reactions. Prof. H. C. Brown (Purdue University, Indiana) seeks to extend the Hammett treatment to

these exceptional systems by obtaining substituent constants incorporating such resonance interactions from the rates of solvolysis of phenyldimethylcarbinyl chlorides. These electrophilic substituent constants have proved useful in quantitatively correlating directive effects in electrophilic aromatic substitution reactions, but a theoretical basis is required for the empirical correlations.

A review of steric effects in nucleophilic aromatic substitution by Prof. N. B. Chapman (University of Hull) covered both primary kinetic steric effects—steric retardation or acceleration of reactions—and secondary steric effects—steric inhibition of mesomerism. Examples of these effects, many from Prof. Chapman's work on nucleophilic aromatic substitution, were given. Although steric acceleration of a reaction is rarer than retardation, the effect is often large when it occurs, for example, in the Smiles rearrangement of 2-hydroxy-2'-nitrodiphenyl sulphone to 2-*o*-nitrophenoxybenzenesulphinic acid. The difficulties in reaching mechanistic interpretations of primary kinetic steric effects were discussed, and attention paid to the influence of the size of the attacking nucleophilic reagent.

Dr. B. M. Wepster (University of Delft) illustrated how the careful interpretation of electronic absorption spectra can lead to a better understanding of chemical data. Thus, the linear relationship between the conjugation band intensities in the ultra-violet spectra and the  $\Delta pK_a$  values for the *p*-nitroanilines

confirms that the inductive and mesomeric effects of the nitro-group operate almost equally in these molecules. The absorption spectra data for nuclear-alkylated anilines and *N*:*N*-dimethylanilines are used to interpret their relative base strengths, while a study of substitutional changes upon the relative base strengths of the nitrogens in 4-aminoazobenzene assists in interpreting the spectra of these compounds in acid solution. The negative inductive effect of the dimethylamino-group and the relative rate-constants for the alkaline deacylation of 4-nitro- and 2:6-dimethyl-4-nitro-acetanilide were also discussed.

Finally, Dr. J. W. Smith (Bedford College, London) discussed dipole moment evidence regarding steric effects in aromatic molecules. Factors which interfere with the coplanarity of a group with the aromatic ring diminish the mesomeric effect and are reflected in the dipole moment. Thus, in *ortho*-substituted nitrobenzenes and *N*:*N*-dimethylanilines,  $\mu(\text{obs.})$  is less than  $\mu(\text{calc.})$ . In anilines, however, an *o*-methyl inhibits mesomerism slightly, while the slightly larger bromine does not. Yet, dipole moment evidence shows that bromine has the greater steric effect upon nitro-, formyl, and acetyl groups. It is inferred, therefore, that the characteristics of the group are important in determining repulsions, and that bromine may have a smaller effective radius with respect to approach by hydrogen than by oxygen, and that the reverse applies to the methyl group.

G. W. GRAY

## OVERSEAS INFORMATION SERVICES

**S**PEAKING in a debate on the Overseas Information Services in the House of Lords on July 9, Lord Adrian stressed the importance of medical and scientific contacts in Commonwealth relations. Fellowships for advanced study and research to able young men and women, if properly used, were the best kind of information service we could give, and Lord Adrian thought we could well spend much more than the present £1 million on such contacts. He referred in particular to the Commonwealth Fund Fellowships, to the British Council's scholarships for postgraduate study and those of the Nuffield and Leverhulme Foundations. Other tributes to the work of the British Council were paid by Viscount Massereene and Ferrard, who, in opening the debate, also referred particularly to the importance of telling the world of our scientific and industrial achievements, Lord Birdwood, Lord Ogmores and by the Earl of Home and the Earl of Gosforth, who spoke for the Government. The Earl of Home assured the House that the Government wishes to strengthen and render more efficient all the information services, and stressed the importance of concentrating expenditure where it was likely to be most effective. In a notable tribute to the British Council he referred to the expansion in the number of Commonwealth students in Britain from between 2,000 and 3,000 in 1946 to 35,000 in 1957, when 11,000 were at universities. He thought, however, that the independent committee of advisers suggested by Lord Birdwood was unlikely to add much to the knowledge of the chief information officers of the Overseas Departments; but he agreed to discuss the proposal and also that of the Drogheda report for a permanent advisory committee with the Chancellor of the Duchy of Lancaster later.

Lord Croft raised the question of the export of British books, particularly scientific and technical text-books, which in countries like India, Pakistan, Burma and Ceylon had largely been displaced by United States text-books, partly in consequence of the aid and information programmes of the American Government. This situation seriously handicapped the sale of British products overseas, and because the distribution of British books and periodicals created a favourable climate for such sales he suggested the Government might, particularly in areas where competition is heaviest, give aid to all central libraries, university libraries and education centres abroad in the selection of British books on particular subjects. For this purpose an initial expenditure of £40,000 and an annual expenditure of £8,000 should service some 400 centres. He suggested also the organization of a limited number of exhibitions of books in areas not served by the British Council and the establishment of a Joint Standing Committee of the British Council and the Central Office of Information on one side, and a voluntary organization of the National Book League and the Publishers' Association on the other, to consider the whole problem. Lord Croft added that about 100,000 copies of books from the United States were being distributed at cut prices and that besides spending 5 million dollars on the translation, publication and distribution of books abroad, the United States, under a low-cost publication programme, had in 1957 launched 4.5 million copies of books in 185 editions and 21 languages. He also pointed out that although we invented the British Book Export Scheme, we did not use it, and because of the Treasury's attitude there were in consequence