The Labile Stereochemistry of Conjugated Systems

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Classical conjugated systems, i.e. those containing alternating single and multiple bonds, have long occupied a prominent place in Organic Chemistry, both for their factual importance and their theoretical interest. Although the stereochemistry of such systems has been extensively studied, it is only in the case of simple benzene compounds, however, that the disposition of the atoms in space may be claimed to have been fully elucidated. The quantitative solution of this problem was achieved by the methods of X-ray and electron diffraction, and of ultraviolet and infrared spectroscopy, and was greatly facilitated by the flatness, symmetry and rigidity of the benzene molecule and many of its derivatives.

Other conjugated systems present considerably greater difficulties to precise analysis for several reasons. The most important of these is that, whereas benzenoid systems approach in varying degrees the state of "perfect" conjugation which exists in benzene itself and in which all the conjugated bonds possess the same amount of double-bond character, electronic interaction in other types of conjugated systems is usually far less complete, so that we must distinguish between bonds essentially single and essentially doubly (or triple) in character. The stereochemistry of partly benzenoid and non-benzenoid conjugated systems therefore consists of two separate, though inter-related parts, that of the single and that of the multiple bonds. Much progress has recently been made with both these aspects, but this article will be concerned mainly with the first—the stereochemistry of the conventional single bonds.

Diphenyl. The spatial arrangement of groups about single bonds (conformation) is generally much more labile than about double bonds (configuration) and the restrictions to free rotation arise from quite different causes. In the case of double bonds, they arise mainly from attractional forces between the unsaturation electrons which normally provide energy barriers exceeding 20 kcal/mol and result in stable geometrical isomers. In the case of "pure" single bonds, on the other hand, the restrictions are due to repulsion forces between non-bonded atoms which normally amount to less than 10 kcal/mol, so that the different conformations are readily interconvertible at ordinary temperatures and cannot be studied by methods requiring their chemical isolation. In the hybrid bonds present in conjugated systems, both factors may come into play. This is the case, for example, in diphenyl (I): \( \pi \) electronic forces will tend to render the molecule uniplanar in order to permit maximum contributions from dipolar resonance structures such as (II) and maximum overlap of the \( \pi \) orbitals, whereas repulsion forces between the \( o \)-hydrogen atoms will tend to make the molecule non-planar.

The conformation of minimum potential energy will therefore have an interplanar angle \( \Theta \) somewhere between 0° and 90°, but we cannot accurately predict its value because we have no precise data for either the maximum resonance energy or the maximum repulsion energy, and we know even less about the variation of these quantities with \( \Theta \). However, in this particular case, we might expect that the resonance energy (ca. 5 kcal/mol) will exceed the repulsion energy between the rather small hydrogen atoms, and therefore that \( \Theta \) will be nearer 0° than 90°. The actual angle has been reported to be about 0° in the crystalline state 1 (where additional, intermolecular forces come into play), but 45° in the vapour phase 2. Some doubts have been expressed about both these values, but it is reasonable to assume that diphenyl is near-planar (\( \Theta < 20° \)) in solution at ordinary temperatures.

The replacement of \( o \)-hydrogen atoms by larger groups will increase the repulsion forces and therefore \( \Theta \), but, as is well-known, two or more \( o \)-substituents are usually required, unless they are of exceptional size, to restrict rotation sufficiently for the existence of resolvable, optically active isomers of reasonable life-time in an asymmetric diphenyl. Thus, the classical chemical method of optical resolution provides a test of the energy barrier to rotation, rather than of the extent of non-planarity in the stable conformations, and represents a relatively crude weapon in investigating the stereochemistry about single bonds. For further progress we must turn to physical methods, most of which yield information about molecular structure in its equilibrium state. Unfortunately, the most precise methods, such as X-ray and electron diffraction are, at present, largely restricted to the solid and gas phase, respectively, and are inapplicable to the study of molecules in solution—i.e. to conditions of particular interest to the chemist. An analytically less precise but experimentally simpler method, which is not subject to this limitation, is absorption spectroscopy. Electronic spectra, in particular, afford a very sensitive index of steric effects in conjugated systems, and make it possible to obtain at least semi-quantitative information concerning interplanar angles.

Ortho-Substituted Diphenyls. One reason why ultraviolet and visible spectral properties are especially sensitive to steric effects is that they are conditioned by differences between the ground state and electronically excited states, and that the steric requirements of the latter are often considerably more exacting than those of the ground state. This is true for example of the 2510Å-band (K-band) of diphenyl, which may be regarded as due to a transition from a ground state in which dipolar structures such as (II) make relatively small contributions, to an excited state in which such structures make relatively large contributions. The introductions of \( o \)-substituents, which cause severe

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hindrance and prevent uniplanarity, will obviously affect the excited state more than the ground state and will raise the energy level of the former with respect to the latter; i.e., the transition energy increases and the K-band is displaced to shorter wave-length. If the steric repulsion is sufficiently great and equals or exceeds the resonance stabilisation, the interplanar angle in the ground state will approach 90° and the two benzene rings will become electronically independent; i.e. the absorption of the system will revert to that of the two separate chromophores. Such phenomena were first observed with the o-methyl diphenyls. The K-Band is shifted to 2350 Å in 2-methyl diphenyl, and to ca. 2150 Å in 2,2'-dimethyl diphenyl, and disappears completely in 2,2',6,6'-tetramethyl diphenyl. From the spectral data, it is possible to construct an energy level diagram (Fig. 1). The resonance stabilisation in the ground state of diphenyl is known from thermo-chemical data to be ca. 5 kcal/mol relative to benzene, and the resonance energy (RE) of the excited state can be deduced to be 34 kcal/mol. Since even one o-methyl substituent will cause steric repulsion exceeding 10 kcal/mol, the RE's for ground states of the mono-, di- and tetra-methyl derivatives will be almost nil, while the RE's of the excited states will be reduced to ca. 21, 10, and 0 kcal/mol, respectively. Although the exact function which connects RE with the interplanar angle is not known, we can make a rough estimate of θ by using the simplest function which passes through the fixed points θ = 0 (maximum RE) and θ = 90° (minimum RE), namely

\[ RE = k \cos^\theta \]  

The values of θ obtained in this way are ca. 40° for mono-, 60° for di-, and 90° for tetra-o-methyl diphenyl.

\[ \begin{array}{c|cccc}
\text{θ} & 0° & 40° & 60° & 90° \\
\hline
\text{RE} & - & 34 & 21 & 10 & 0 \\
\text{Excited states} & & & & & \\
\hline
\text{Ground states} & 2,000 Å & 2,350 Å & 2,350 Å & 2,125 Å & 2,000 Å \\
& 14 kcal & 14 kcal & 14 kcal & 13.3 kcal & 14 kcal \\
& \text{and 14 kcal} & \text{and 14 kcal} & \text{and 14 kcal} & \text{and 14 kcal} & \text{and 14 kcal} \\
\end{array} \]

Fig. 1.—Electronic transitions between non-planar ground states and non-planar excited states. (Energy level diagram for diphenyl and ortho-methyl diphenyl.)

Ortho-Bridged Diphenyls. A different kind of situation can arise if steric hindrance to uniplanarity is relatively small, either because the repulsion forces are weak or because they are compensated by bonding forces which tend to keep the system planar. A good example of the latter type is provided by ortho-bridged diphenyls such as 9,10-dihydrophenanthrene, dihydrodibenzoxepin and dihydrodibenzazepinium derivatives. The ultraviolet spectra of these compounds are quite different from those of o,o'-disubstituted diphenyls; the "diphenyl"-bands show the usual bathochromic, instead of hypsochromic, displacements and only the intensities are decreased as compared with diphenyl (table I). The absence of any usual λ shifts (< 50 Å) means that the transition energy, and therefore the energy levels of the ground and excited states, are almost unchanged (< 3 kcal) by any steric effects, but the decrease in ε shows that the transition probability is reduced. According to classical theory, transition energy and probability are normally interdependent, and a change in ε without change in λ must therefore be due to a sterically conditioned change in selection rules: the transition has evidently become partly "forbidden". We can interpret this in the following way. Let us call the mean interplanar angle Θ₁ in the ground state, and Θ₂ in the excited state. Since the amount of double bond character of the single bond joining the two conjugated groups, and the resonance energy are increased in the excited state (see above), Θ₂ will be rather smaller than Θ₁. Now it is a fundamental principle, formulated by Franck and Condon, that since the motion of electrons is very much faster than that of atomic nuclei, interatomic distances (and therefore, interplanar angles) cannot change during an electronic transition; in other words, transitions can only occur along vertical lines in the potential energy diagram (Fig. 2). Hence a molecule with θ = Θ₁ cannot pass di-

\[ \begin{array}{c|c}
\text{INTERPLANAR ANGLE} & \Theta_1, \Theta_2 \\
\hline
\text{Electronic excited state} & \text{Transitions "forbidden"} \\
\text{Potential energy curves} & \text{Transitions "allowed"} \\
\text{Ground state} & \Theta_2 \\
\end{array} \]