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The Configuration of Diphenyl in the Crystalline and in the Vapour States: A Simple Non-bonded H-H Potential Function

By

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Electron diffraction shows that in the vapour the phenyl rings of diphenyl are inclined at about 42° . This is a compromise between the $2p_z$ -orbital overlap, which tends to keep the whole molecule planar, and overcrowding of the 2:2' and 6:6' hydrogen atoms which causes twisting of the rings to reduce the steric repulsion. A potential function, having an exponential form, has been derived, which gives a minimum at the observed angle.

La diffraction électronique indique qu'en vapeur les anneaux phényles du diphényl s'inclinent à 42° approximativement. Cet angle est un compromis entre le recouvrement des orbitales $2p_z$ qui tend à maintenir plan la molécule entière, et l'encombrement des atomes d'hydrogène 2:2' et 6:6' qui font tordre les anneaux pour réduire la répulsion stérique. On a dérivé une fonction potentielle, d'une forme exponentielle, qui a un minimum à l'angle observé.

Die Elektronenbeugung zeigt, daß die beiden Ringe des Diphenyls im Gaszustand um einen Winkel von etwa 42° gegeneinander verdreht sind. Dieser Zustand stellt einen Kompromiß dar zwischen der Überlappung der p_z -Orbitale einerseits, die das ganze Molekül planar zu halten sucht, und der Pressung der van der Waals-Radien der 2,2' und 6,6'-Wasserstoffatome andererseits, die die Ringe aus der gemeinsamen Ebene herausdreht, um die sterische Hinderung abzumindern. Für die potentielle Energie wurde eine e -Funktion mit einem Minimum am beobachteten Winkel hergeleitet.

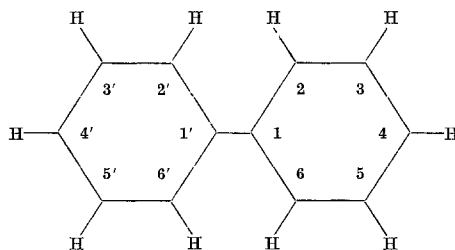
X-ray diffraction studies show that in the crystalline state diphenyl is planar [9] or very nearly so [12], but electron diffraction results [1] indicate that in the vapour phase there is an angle of about 42° between the planes of the phenyl rings. Since in the vapour the molecules may be regarded as free from mutual interaction the configuration in this state may be regarded as an equilibrium compromise between the tendency towards planarity, which is promoted by p_z -orbital overlap across the bond between the rings and which favours a lowering of π -electron energy, and that towards non-planarity which favours reduction of steric repulsion energy between the overcrowded hydrogen atoms 2 and 2', 6 and 6'.

1. Calculation of π -electron delocalisation energy across the interphenyl bond

For the planar diphenyl molecule it is a simple matter to calculate the total energy of the π -molecular orbitals by the usual Hückel approximation, particularly if group theoretical methods are used to factorise the 12th-order secular determinant of C_{2v} symmetry into the two quartics of the A_1 and B_1 symmetry classes and the two quadratics of the A_2 and B_2 classes. When the rings are not coplanar the interactions β_{rs} between neighbouring atomic orbitals on carbon atoms r, s remain unaltered except for that, $\beta_{1,1'}$, between the orbitals on atoms 1

and 1', which becomes $\beta_{1:1'} \cos \theta$, θ being the angle by which one ring has been rotated about the axis 4:1:1':4' with respect to the other. It follows that, within the limits of the Hückel approximation ($\beta_{rs} = 0$ if r and s are not neighbours) the A_2 and B_2 determinants remain exactly as for the completely planar molecule since they do not involve the orbitals on the two-fold axis of the twisted structure, and the A_1 and B_1 determinants require only the multiplication of $\beta_{1:1'}$ by $\cos \theta$. Thus pseudo- C_{2v} symmetry remains.

Now the interphenyl bond, as measured by X-ray crystal analysis, is 1.50 Å long [9, 12] whereas the electron diffraction spectrum [1] is interpreted as showing its length to be 1.48 Å. DEWAR and SCHMEISING [7] believe that the



length of apure σ -bond between sp^2 hybridised carbon atoms is 1.48 Å and this is supported by various other pieces of evidence [10, 13]. We have assumed, therefore, that the small difference of 0.02 Å is significant, that the bond 1:1' is stretched a little in the crystalline state to relieve the overcrowding of the hydrogen atoms at 2 and 2' and at 6 and 6', and that this extension persists for values of θ not greater than 20°, i.e. \approx half of the observed 42° twist [1].

To calculate the π -electron energy levels for the molecule when $C_1 - C_{1'} = 1.48$ and 1.50 Å the corresponding β -values were inferred from the LONGUET-HIGGINS and SALEM [11] relationship as $0.750 \beta_0$ and $0.710 \beta_0$ respectively, β_0 being the interaction integral appropriate to the bond length in benzene, to which the ring bonds of diphenyl approximate fairly closely.

The total π -electron energy is then given, for the ground state, by

$$\mathcal{E}^e(\theta) = 2 \sum_{i=1}^6 \varepsilon_i(\theta) = 12 \alpha - 2 \beta_0 \sum_{i=1}^6 x_i(\theta),$$

where $x_i(\theta)$ is the "Hückel number" (negative for binding orbitals) of the i -th molecular orbital, summation being over the six doubly occupied levels. The π -electron energy of two isolated benzene molecules in their ground states is $12 \alpha + 16 \beta_0$ and hence the "energy of delocalisation" across the bond 1:1', i.e., the π -electron stabilisation gained by untwisting the molecule, is

$$\varepsilon_\pi(\theta) = - \left[2 \sum_{i=1}^6 x_i(\theta) + 16 \right] \beta_0.$$

Fig. 1 gives the plot of $\varepsilon_\pi(\theta)$ against θ for $0 \leq \theta \leq \pi/2$; that the curve is closely

sinusoidal is shown by the degree of coincidence with the fitted curve (broken line)

$$\varepsilon_\pi(\theta) = 0.196 \beta_0 \cos^2 \theta = -6.375 \cos^2 \theta \text{ kcal/mol} \quad (1)$$

when β_0 is given [8] the value -32.5 kcal/mol.

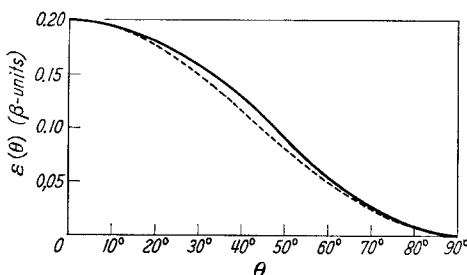


Fig. 1. $\varepsilon_\pi(\theta)$ against θ

2. The Potential Function for Repulsion between the Hydrogen Atoms

The form of the repulsive potentials between the hydrogen atoms at carbons 2 and 2' and at carbons 6 and 6' is not known with certainty. It is discussed for some similar situations by COULSON and HAIGH [4]. Most authors use a BUCKINGHAM "6-exponential" function [5]

$$V(r) = -Ar^{-6} + Be^{-cr} \quad (2)$$

in which r is the distance between the unbound hydrogens. We have worked, however, in terms of the variable θ and since $V(\theta)$ clearly decreases with increasing θ for $|\theta| < \pi/2$, we shall assume that it may be expressed by an exponential function

$$V(\theta) = V_0 \exp(-n\theta^{2m}) \quad (3)$$

the shape of which may be adjusted by means of the parameters n and m , m being integral. We have chosen this type of function for its simplicity and because it is symmetrical about a maximum at $\theta = 0$ as the problem requires. V_0 is the empirical

barrier height for internal rotation due to the overcrowded hydrogen atoms alone, though this cannot be measured in the normal way for diphenyl because of the attractive contribution by the π -electrons to the observed barrier. We may, however, estimate it as follows. The energy difference between *cis* and *trans* butadiene is found [2] from thermodynamic considerations to be 2.30 kcal/mol. Since the π -electron energy in the two isomers is the same within the approximations of the

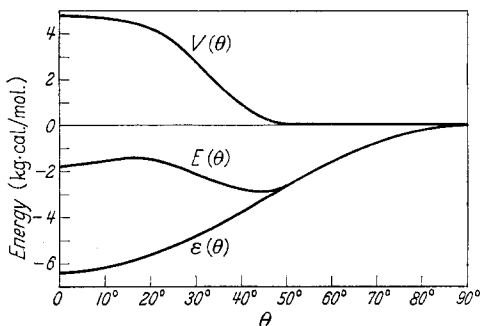


Fig. 2. $V(\theta)$, $\epsilon_{\pi}(\theta)$, $E(\theta)$ against θ

Hückel theory, this difference must be accounted for by steric repulsions between the hydrogen atoms at the 1 and 4 positions of *cis* butadiene since in the *trans* compound no two hydrogen atoms approach within twice their van der Waals radius. Now the distance between the 2 and 2' and the 6 and 6' hydrogen atoms in diphenyl is very close to that in *cis*-butadiene. Hence we take V_0 in the former to be just twice the steric hindrance barrier height in the latter. (3) therefore becomes

$$V(\theta) = 4.60 \exp(-n\theta^{2m}) \text{ in kcal/mol.} \quad (4)$$

3. Minimisation of the Total Energy

That portion of the total energy of diphenyl which is dependent on θ is then given as the sum of (1) and (4)

$$E(\theta) = 4.60 \exp(-n\theta^{2m}) - 6.375 \cos^2 \theta. \quad (5)$$

Differentiating and using the fact that there is a minimum at $\theta = 42^\circ$ we have

$$-9.20 mn \times 0.7330^{2m-1} \exp(-0.7330^{2m}n) + 6.375 \sin 84^\circ = 0. \quad (6)$$

For $m = 1$ no value of n makes $E(\theta)$ a minimum at $\theta = 42^\circ$ but to each greater integral m there corresponds a value of n satisfying (6). With $m = 2, 3, 4, 5$

$V(\theta)$ has a flat portion with $|\theta|$ less than 20° and decreases almost to zero at $|\theta| = 45$ or 50° . We have selected (7), with $m = 2$,

$$V(\theta) = 4.60 \exp(-7.393 \theta^4) \quad (7)$$

as the most likely of this family of curves since it has the shortest flat portion ($|\theta| < 10^\circ$). With $m = 3, 4, 5$ $n \approx 18, 40, 80$ respectively. Curve (7) is shown in Fig. 2 along with $\epsilon_\pi(\theta)$, the π -electron energy across the bond 1:1', and the resultant energy $E(\theta)$. We note that besides the minimum in $E(\theta)$ at 42° a shallower minimum is found at 0° . This may account for the planarity in the crystalline state since only 1 kcal/mol need be supplied by the crystal forces to convert the twisted to the planar configuration.

4. Root Mean Square Amplitude of Twisting

Taking the potential well in $E(\theta)$ at $\theta \approx 42^\circ$ as shown in Fig. 2, we may attempt to estimate the root mean square amplitude of the twisting of the phenyl rings with respect to each other by assuming the motion to be simple harmonic and calculating the force constant κ

$$V(\theta) = \frac{1}{2} \kappa \theta^2. \quad (8)$$

The best fit of (8) to $E(42^\circ)$ is with $\kappa = 0.003$ from which, using CRUICKSHANK'S relationship [6]

$$\overline{\Phi}^2 = \frac{2kT}{\kappa}$$

where k and T are the Boltzmann constant and the temperature, the mean square amplitude $\overline{\Phi}^2$ is found. Because of uncertainty in fitting (8) to (5) there is an appreciable uncertainty in κ and hence in $\overline{\Phi}^2$ but a smaller uncertainty in $(\overline{\Phi}^2)^{\frac{1}{2}}$, for which the value 28° is found, corresponding to a root mean square twist of each ring of 14° in opposite directions. The only experimental evidence which can be set alongside this calculation seems to be the inferences of ALMENNINGEN and BASTIANSEN [1] that the probability of finding the phenyl rings at any angle θ in the neighbourhood of 42° is quite large and that to reduce this probability to one half of the equilibrium probability the phenyl rings would need to be rotated through 17° in opposite directions.

5. Non-Bonded Repulsion as a Function of r

It is of interest to express the repulsive potential (7) in terms of the distance r between a pair of overcrowded hydrogen atoms. Using the bond lengths $C_1C_1' = 1.490$, $C_1C_2 = 1.398$, $C_2H_2 = 1.084$ Å and the angle $C_1C_2H_2 = 120^\circ$

$$r = (12.4949 - 9.2397 \cos \theta)^{\frac{1}{2}}. \quad (9)$$

When (9) is substituted into (7) we have

$$V(r) = 4.60 \exp \left\{ -7.393 [\cos^{-1} (1.3523 - 0.1082 r^2)]^4 \right\}. \quad (10)$$

The curve $V(r)$ is shown in Fig. 3. As for most repulsive potential functions it rapidly approaches zero, doing so, in fact, rather abruptly at approximately 2.6 \AA , i.e., at just over twice the van der Waals radius of hydrogen (1.2 \AA).

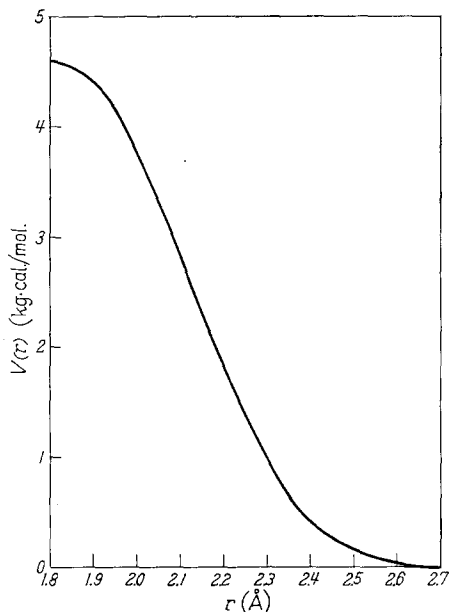


Fig. 3. $V(r)$ against r

6. C-H bending

The shoulder in $V(\theta)$ arises, of course, from the selection of a potential of the form (3). In planar and nearly planar molecules some relief of steric repulsion can be achieved by the bending of the $C-H$ bonds (in conjunction with the stretching of the $C-C$ bond) and would also have the effect of lowering (flattening) $V(\theta)$ at low θ . That such bending does occur is revealed by the accurately determined crystal structures of certain overcrowded molecules, e.g., chrysene [3].

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