The Conformational Problem of Biphenyl in Solution as investigated by the Liquid Crystal Nuclear Magnetic Resonance Spectrum of 3,3′,5,5′-Tetrachlorobiphenyl

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The interpretation of the ^{1}H n.m.r. spectrum of a *meta*-substituted biphenyl (3,3′,5,5′-tetrachlorobiphenyl) dissolved in the nematic phase of a liquid crystalline solvent showed unambiguously that in solution it has neither a planar structure nor free rotation but exists in a twisted conformation. A fairly accurate measurement of the twisting angle could also be obtained (34° 20′), the experimental error being similar to that reported in the electron diffraction studies of the vapour phase. The effects of the substituents and of the nematic solvent upon the conformation are discussed and the conclusion is reached that they are rather small and acting in opposite directions. Biphenyl is thus expected to have a similar dihedral angle in solution.

THE conformation of biphenyl has been the subject of a large number of experimental and theoretical investigations throughout the last 40 years. It has been unambiguously ascertained by means of *X*-ray diffraction [1-3] that biphenyl is planar in the solid state whereas electron diffraction methods showed that in vapour phase the two phenyl rings are twisted [4] by 42°.[5] A number of theoretical investigations [6,7] have been also published to rationalise the structure of biphenyl, the most recent giving good agreement with the results for the vapour phase.

On the other hand there is disagreement among various authors as to the conformation of biphenyl in the liquid phase or in solution, as the techniques employed for studying this problem were not well suited to giving structural information. I.r. and Raman spectra of biphenyl and deuteriobiphenyls were claimed to give evidence for the planarity in solution or in the liquid phase [8] although slightly twisted conformations were not excluded.[9] It has however been pointed out that the interpretation or i.r. spectra of biphenyl does not allow a reliable determination of the twisting angle, although evidence may be obtained in favour of a non-planar structure.[10] A recent reinvestigation of both i.r. and Raman spectra suggested [11] a value of the twisting angle of 45 ± 15°; the uncertainty however is exceedingly large.

U.v. spectroscopy has been also employed for these investigations; a planar conformation was earlier suggested [12] whereas some degree of twisting was later proposed (18—23°).[13,14] E.s.r. studies of the radical anion reached opposite conclusions. McLachlan [15] favoured a planar structure whereas Möbius [16] suggested a 38° twisting angle as better reproducing the experimental data. The dipole moments of some biphenyls have been interpreted on the basis of 30—40° twisting angle [17] in agreement with the data for the depolarisation of Rayleigh scattered light (24—31°),[18] while measurements of molar Kerr constants seemed to support a planar structure [19] as did light scattering and magnetic anisotropy investigations.[20] Finally it is worth mentioning that n.m.r. studies of biphenyl in solution did not afford reliable information on the geometry; attempts to obtain information from chemical shifts failed since it was not

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possible to distinguish between free rotation and twisted structures.[21]

Because of the unsatisfactory knowledge of the conformation of biphenyl in solution we attempted a new approach to the problem based, as were the *X*-ray and electron diffraction methods, only on experimental evidence. For this purpose n.m.r. spectroscopy in the nematic phase of a liquid crystalline solvent was employed.

RESULTS AND DISCUSSION

(a) *Basic Method.*—It is known that the n.m.r. spectra of molecules dissolved in partially oriented media allow the measurement of those nuclear dipole–dipole interactions (D_{ij}) which are not detectable in isotropic solutions because they are averaged out by molecular tumbling.[22] Actually in the Hamiltonian (1) describing the magnetic resonance spectrum of an oriented molecule the numerical values of D_{ij} are usually larger than chemical shifts ($\Delta\nu_{zz}{}^i$) and direct couplings (J_{ij}). In

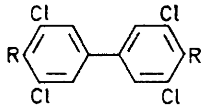
$$\mathscr{H} = \sum_i \nu_{zz}{}^i I_z{}^i + \sum_{i>j} J_{ij}\boldsymbol{I}^i . \boldsymbol{I}^j + \tfrac{1}{2}\sum_{i>j} D_{ij}(3I_z{}^iI_z{}^j - \boldsymbol{I}^i . \boldsymbol{I}^j) \qquad (1)$$

the present treatment no screening anisotropy has been allowed for the Zeeman interaction ($\nu_{zz}{}^i$), an approximation which is well justified for proton spectra. As the dipolar couplings D_{ij} depend upon the geometry and orientiation of the molecule but not on the electronic distribution, fairly accurate determination of molecular shapes can be achieved.[23] The basic equation linking the experimental D_{ij} values to the atomic co-ordinates and orientational parameters has been established.[24] The motional constants in the spherical harmonic formulation [24] are also related to the elements of the ordering matrix $\boldsymbol{S}$ introduced by Saupe.[25]

The main source of inaccuracy in such an experimental approach concerns the intrinsic differences between the liquid crystalline media and the isotropic solvents,[26] for one cannot in principle rule out the possibility of distortion of molecules when they are dissolved in the nematic phase. In cases of rigid structures many investigations have shown that, within the accuracy required for most chemical purposes, there is no significant difference between the results for liquid crystals and from other structural techniques.[23,27] Even when conformational isomers are possible the conclusions derived from liquid crystal n.m.r. investigations do not seem to contradict the results of measurements in isotropic media.[28] However in cases of flexible molecules such as biphenyl, flattening of the angles analogous to those observed in the solid with respect to the vapour phase cannot be excluded. These effects have been inferred, in some cases, from e.s.r. studies of radicals in the nematic phase;[29,30] however the amount of flattening required to explain the increase of the hyperfine splitting constants in the nematic phase with respect to the isotropic solvent has been estimated as only a few degrees.[30]

Another source of approximation that could not be avoided arises from the fact that the nematic phase n.m.r. spectrum of biphenyl as such could not be obtained.[31] To overcome this difficulty 3,3′,5,5′-tetrachlorobiphenyl (I) was employed. The number of protons being reduced from ten to six, a well resolved spectrum (Figure 1) could be obtained.

meta-Substitution and the electronic properties of the chlorine atoms prevent significant deviations from occurring with respect to the structure of unsubstituted biphenyl; this assumption is proved by the vapour phase electron diffraction measurement [5] of the analogous 3,3′,5,5′-tetrabromobiphenyl whose twisting angle (49 ± 7°) is almost equal, within experimental error, to that of biphenyl measured under analogous conditions (45 ± 10°).



(I) R = H

(II) R = Cl

As the effects of the liquid crystalline solvent and of *meta*-substitution are expected to be rather small and, furthermore, to act in opposite directions, it is reasonable to predict that the present investigation would lead, in principle, to a determination of the twisting angle of biphenyl in solution which is more reliable than those previously reported.

(b) *Spectral Analysis and Structure Determination.*—In order to ease the calculation of the D_{ij} values from

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the spectrum of Figure 1 we made use of 3,3′,4,4′,5,5′-hexachlorobiphenyl (II). Only two dipolar couplings are required to define its spectrum and they could be easily determined. The spectral data of compound (II) dissolved in *N*-(*p*-ethoxybenzylidene)-*p*-n-butylaniline (EBBA) at 47 °C are reported in Table 1. Assuming an arbitrary structure (we actually used a planar and a 40° twisted conformation) a rough evaluation of the two ordering matrix elements S_{zz} and $S_{xx} - S_{yy}$ was obtained; these values were employed as a starting point to estimate the D_{ij} couplings to be used as input data to analyse the spectrum of (I). A number of $S_{zz} : (S_{xx} - S_{yy})$ ratios were thus used with the limitation that the values do not exceed that obtained from the corresponding structure of (II), as the absence of the two chlorine atoms in the *para*-positions reduces the orientation of the molecular *z*-axis with respect to the applied magnetic field. None of the theoretical spectra obtained with this method approached the experimental one as long as a planar structure was assumed, while one among those derived from the twisted conformation matched a sufficient number of lines to allow the use of a best-fitting process which eventually provided the data collected in Table 2.

TABLE 1

Spectral parameters (Hz) of the 100 MHz downfield half-spectrum of 3,3′,4,4′,5,5′-hexachlorobiphenyl (II) in EBBA at 47 °C

Experimental frequencies	−896·9	−585·1	−360·9	−151·0
Calculated frequencies	−894·2	−587·2	−361·4	−153·5
Intensities	4·0	2·0	6·0	2·0

Chemical shift	0·0 ± 0·7
$D_{22'} = D_{26'} = D_{2'6} = D_{66'}$	−493·8 ± 0·7
$D_{26} = D_{2'6'}$	−204·7 ± 0·7

Four possible situations may in principle be expected for the biphenyl and they have to be examined to see whether the liquid crystal n.m.r. spectrum allows an unambiguous choice.

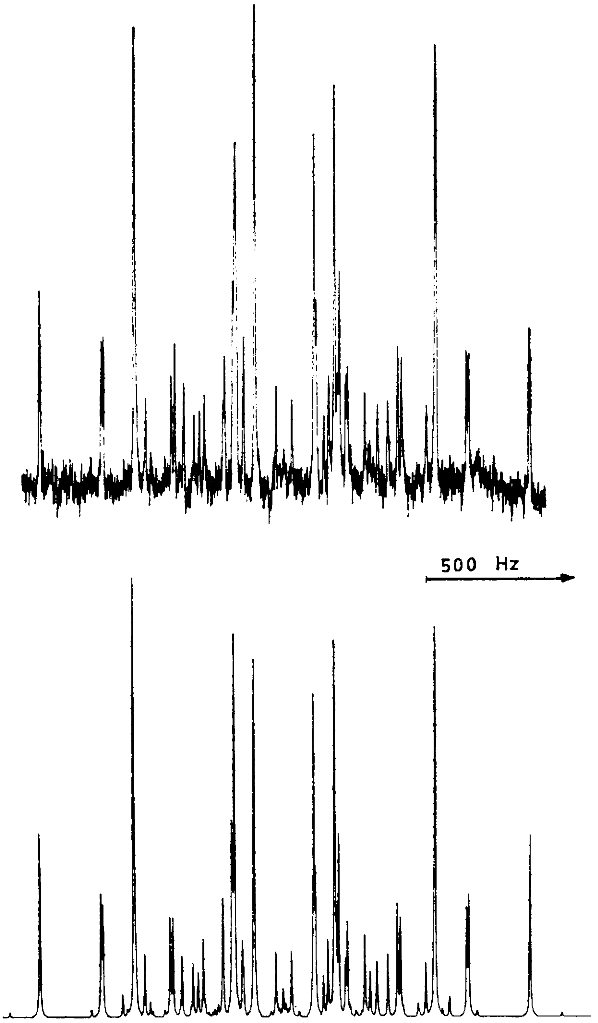

FIGURE 1 Upper trace: 100 MHz spectrum of 3,3′,5,5′-tetrachlorobiphenyl (I) in NEOAB at 78 °C; lower trace: computer simulated spectrum obtained using the parameters of Table 1 and a Lorentzian line shape with a half height width of 3·5 Hz

TABLE 2

Experimental and computed D_{ij} values (in Hz) of the 100 MHz spectrum of 3,3′,5,5′-tetrachlorobiphenyl (I) in NEOAB at 78 °C. Chemical shift of 4-H = 4′-H is 5·5 ± 0·7 Hz downfield with respect to 2-H = 2′-H = 6-H = 6′-H assumed 0. The value of $J_{24} = J_{2'4'} = J_{46} = J_{4'6'}$ was kept equal to 2·00 Hz as in isotropic solvents; $J_{26} = J_{2'6'}$ was also assumed equal to 2·0 Hz

		Computed			
	Experimental	$\Theta = 34° 20'$	$\Theta = 0°$	$\Theta = 90°$	Free rotation
$D_{22'} = D_{26'} = D_{2'6} = D_{66'}$	−224·3 ± 0·4	−224·3	−268·2	16·8	−236·1
$D_{24} = D_{2'4'} = D_{46} = D_{4'6'}$	−330·6 ± 0·4	−330·2	−120·1	−66·3	−80·2
$D_{24'} = D_{2'4} = D_{46'} = D_{4'6}$	−125·6 ± 0·4	−126·8	−26·2	−31·7	−38·3
$D_{26} = D_{2'6'}$	−259·8 ± 0·7	−259·8	−311·9	53·3	64·5
D_{44}	−35·0 ± 0·8	−34·8	−3·8	−10·4	−12·6
R.m.s. deviation (Hz)		0·6	109·4	217·8	187·7
S_{zz}		0·115	0·013	0·034	0·041
S_{xx}		−0·228	−0·117		

If the molecule exists in a planar structure (D_{2h} symmetry point group) or in a conformation twisted by <90° (D_2) two ordering matrix elements (S_{zz} and $S_{xx} - S_{yy}$) are required to describe the orientation [32] whereas in the case of free rotation ($D_{\infty h}$) or 90° twisted conformation (D_{2d}) only S_{zz} is needed.[33] In all four cases the problem is overdetermined provided that the positions of the hydrogen atoms within each of the two benzene rings are known.

For the planar situation a complete set of data has been

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obtained[2] for the solid state. However, the parameters of the *ortho*-hydrogen atoms cannot be used for other conformations since the distortions due to overcrowding are likely to disappear when the two rings are not coplanar. Accordingly for the three non-planar models the basic geometry of ref. 3 was used and the CH bonds (1·08 Å in length[34]) were assumed to bisect the corresponding phenyl ring angles. A slight difference has been also observed between the phenyl–phenyl bond in the solid (1·506 Å[3]) and in the vapour phase (1·489 Å[5]); this fact, which has also been theoretically justified,[7] was found however to be almost negligible in affecting the results of this investigation.

Before searching for the twisting angle we must check that a free rotation model may be discarded; accordingly the terms were numerically averaged over 0 and 2π and used to fit the five experimental couplings. As appears from Table 2 the deviation between experimental and computed values allows us unambiguously to exclude the possibility of free rotation. Also the planar and 90° twisted structures turned out to be in definite disagreement with the experimental data whereas the conformation with the two phenyl rings twisted by 34° 20′ reproduces the D_{ij} values within experimental error (Table 2). In Figure 2 the root mean square deviations between calculated and experimental D_{ij} couplings (Δ) are plotted against the twisting angle (Θ°); the trend is such as to allow a very accurate determination, as differences of $<0{\cdot}5°$ would make the computed values exceed the experimental error. The co-ordinates of the hydrogen atoms corresponding to the best fit (34° 20′) are reported in Table 3; they were obtained by twisting the biphenyl skeleton of ref. 3. The dependence of the minimum upon the choice of the co-ordinates was checked by employing the previously mentioned basic geometries and it was found not to exceed 60′.

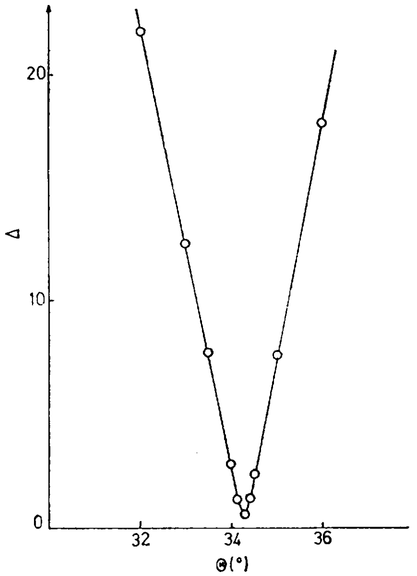
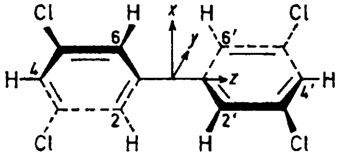


FIGURE 2 Dependence of the root mean square deviation (Δ/Hz) between calculated and experimental dipolar couplings upon the twisting angle (Θ) of the phenyl rings in 3,3′,5,5′-tetrachlorobiphenyl (I)

TABLE 3

Co-ordinates (Å) of the hydrogen atoms of compound (I) used to obtain the best set of computed D_{ij} values. They correspond to the geometry of ref. 3 twisted by 34° 20′ with the CH bonds (1·08 Å) bisecting the corresponding carbon–carbon angles



(I)

Position	z	y	x
2-H	$-0{\cdot}92_3$	$-2{\cdot}03_3$	$-0{\cdot}62_7$
2′-H	$0{\cdot}92_3$	$-2{\cdot}03_3$	$0{\cdot}62_7$
4-H	$-4{\cdot}62_4$	0·000	0·000
4′-H	$4{\cdot}62_4$	0·000	0·000
6-H	$-0{\cdot}92_3$	$2{\cdot}03_3$	$0{\cdot}62_7$
6′-H	$0{\cdot}92_3$	$2{\cdot}03_3$	$-0{\cdot}62_7$

Conclusions.—It has been possible to determine that 3,3′,5,5′-tetrachlorobiphenyl (I) in a nematic solution is twisted by 34° 20′; the accuracy of this measurement cannot be transferred however to unsubstituted biphenyl owing to the small perturbations induced by the chlorine atoms and by the peculiar kind of solvent employed. This value probably represents the lowest limit for biphenyl, as the slight flattening effect of the nematic solvent cannot be excluded; accordingly biphenyl in solution is expected to exist in a twisted conformation with an angle (34°) close to that observed in the vapour phase by means of electron diffraction.

In the present investigation, as in the electron diffraction studies, the implicit assumption has been made that the molecules only populate the most stable conformation. Obviously, because of the possibility of internal rotation, the inclusion in the calculations of a potential curve would lead to more meaningful results; such an investigation, which is particularly advisable as the energy barrier is expected to be rather low, is now in progress.

EXPERIMENTAL

Spectral Measurements.—The 100 MHz spectra of compound (I) in 4,4′-bis-n-hexyloxyazoxybenzene (NEOAB) at 78 °C and of compound (II) in EBBA at 47 °C were recorded on a JEOL PS 100 spectrometer in the sweep field mode with external lock. The spectral analysis was performed by the LAOCN computing program[35] modified in order to introduce the dipolar Hamiltonian (LAOCOONOR).[36] The eight lines of the spectrum of compound (II) were reproduced with a root mean square deviation of 2·0 Hz and the 43 lines of the spectrum of compound (I) with a root mean square deviation of 2·4 Hz.

To find out the conformation of compound (I) the atomic co-ordinates were fed into a program which computed the

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motional constants best fitting the experimental D_{ij} values. The twisting angle was changed until the minimum deviation (0·6 Hz) between experimental and computed couplings was reached. The same program was also used in reverse to obtain from the data for compound (II) an approximate estimate of the D_{ij} values of compound (I) to be fed in the first part of LAOCOONOR. All the programs were run on a CDC 6600 computer. The value of the direct J_{24} coupling (2·00 Hz) was obtained by analysing the spectrum of compound (I) in CCl_4 as an AB_2 group; to J_{26} which could not be derived from the spectral analysis [37] the same value was attributed since both are J_{meta} couplings. As only one value for $D_{22'}$, D_{26}, $D_{2'6'}$, and $D_{66'}$ was experimentally observed in the spectrum of compound (I), we considered two equivalent conformations [38] with either 2-H-2′-H or 2-H-6′-H *syn* in a 1 : 1 ratio; in either form the same weight was attributed to all five D_{ij} couplings.

Syntheses.—3,3′,5,5′-*Tetrachlorobiphenyl* (I). To an ether solution of n-butyl-lithium (0·05 mol. equiv.) an equimolar amount of 3,5-dichloroiodobenzene (13·6 g) [39] and freshly prepared Cu_2Cl_2 (5 g) were added. After refluxing for 18 h the mixture was poured onto ice–water with vigorous stirring and acidified with hydrochloric acid. The organic layer was separated and the aqueous solution was again extracted with ether. The organic fractions were dried and, on removing solvent, the product (70—80%) was obtained, m.p. 165—167 °C (sublimed) (from ethyl alcohol) (lit.,[39] 162 °C), δ (CCl_4) 7·338 (*J* 2 Hz, 2-H) and 7·306 (*J* 2 Hz, 4-H) (Found: C, 49·2; H, 1·82; Cl, 48·5. Calc. for $C_{12}H_6Cl_4$: C, 49·35; H, 2·07; Cl, 48·6%).

3,3′,4,4′,5,5′-*Hexachlorobiphenyl* (II). This was prepared in the same way using 3,4,5-trichloroiodobenzene as starting material. The product sublimes at 100 °C and 0·3 mmHg, m.p. 204—205 °C (from acetic acid) (lit.,[39] 198 °C), δ (CCl_4) 7·52 (Found: C, 40·1; H, 1·12; Cl, 59·3. Calc. for $C_{12}H_4Cl_6$: C, 39·95; H, 1·12; Cl, 58·95%).

3,4,5-*Trichloroiodobenzene*. This was prepared from 3,4,5-trichloroaniline [40] by a conventional method in almost quantitative yield, m.p. 55—56 °C (from ethyl alcohol), δ (CCl_4) 7·66 (Found: C, 23·3; H, 0·68; Cl, 34·4; I, 41·0. Calc. for $C_6H_2Cl_3I$: C, 23·45; H, 0·66; Cl, 34·6; I, 41·3%).

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