^{1}H Nuclear Magnetic Resonance and *X*-Ray Study of Dihedral Bond Angles in the *Gauche* O·CH$_2$·CH$_2$·O Moiety of Cyclic 7,8-Dihydrodibenzo[*f,h*]-[1,4]dioxecin

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The ^{1}H n.m.r. spectra of the CH$_2$·CH$_2$ groups in two *ortho, ortho'*, ·CH$_2$·X·CH$_2$·CH$_2$·X·CH$_2$· bridged biphenyl derivatives (I) (X = –O–) and (II) (X = MeN<) have been analysed. A set of four coupling constants has been derived: $^3J_{AA'}$, $^3J_{BB'}$, $^3J_{AB'}$ (= $^3J_{A'B}$), and $^2J_{AB}$. The $^3J_{HH}$ values were found to be only slightly temperature- and solvent-dependent.

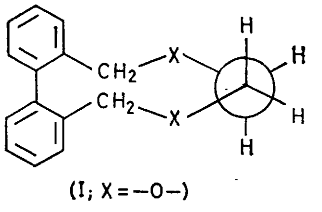
These coupling constants were used for a study of the geometry of the ·X·CH$_2$·CH$_2$·X· moiety of these molecules in solution. Dihedral bond angles were calculated by use of various known $^3J_{HH}/\phi$ relationships and the results compared with those obtained from an *X*-ray study of the ·O·CH$_2$·CH$_2$·O bridged derivative (I).

Crystals of (I) are orthorhombic, space group *Aba*2, with $Z = 4$ in a unit cell of dimensions $a = 11.871$ (1), $b = 13.882(2)$, $c = 7.875(2)$ Å. The structure was determined by direct methods and refined by least-squares techniques to R 0.033 for 410 observed reflections. The molecules have C_2 symmetry. Dihedral bond angles between the coupled proton pairs are 31(4), 77(6), and 176(8)°.

The $^3J_{HH}/\phi$ relationship predicts successfully the deviation from the idealized value of 60° for the *gauche*-oriented proton pairs in (I).

MUCH interest exists in the relation between spin–spin coupling constants of vicinal protons, $^3J_{HH'}$ in HCCH' systems and dihedral bond angles, ϕ. Several empirical and theoretical $^3J_{HH'}/\phi$ relations have been suggested [1] and employed [2] for the elucidation of molecular geometries in solution directly from measured $^3J_{HH'}$ values.

Recently we isolated [3] two biphenyl derivatives (I) and (II) in which the *ortho*-positions of the two phenyl rings are linked by either a ·CH$_2$·O·CH$_2$·CH$_2$·O·CH$_2$· or a ·CH$_2$·N(Me)·CH$_2$·CH$_2$·N(Me)·CH$_2$· chain. These chains block rotation of the two phenyl rings with respect to each other. Furthermore, space-filling models of these molecules indicate that the ring conformers cannot pass into their mirror images because of the presence of the biphenyl system in the ten-membered ring. These structural features make compounds (I) and (II) particularly suitable for an experimental verification of the known $^3J_{HH'}/\phi$ relationships.



(I; X = –O–)
(II; X = >NMe)

This paper reports the results of an ^{1}H n.m.r. study of both (I) and (II) as well as of the use of the $^3J_{HH'}/\phi$ relationships for the calculation of the dihedral bond angles in the ·X·CH$_2$·CH$_2$·X· grouping. The angle values obtained are compared with those resulting from the *X*-ray study of (I).

EXPERIMENTAL

Synthesis of 7,8-*Dihydrodibenzo*[f,h][1,4]*dioxecin* (I) *and* 7,8-*Dihydro*-6,9-*dimethyldibenzo*[f,h][1,4]*diazecin* (II).—A solution of the bis-Grignard 1,2-bis[2-(bromomagnesio)-benzyloxy]ethane (obtained from the reaction of 88.3 mg at Mg with 30 mmol of tetrahydrofuran [4]) was added at –20 °C to a suspension of 25.7 mmol of anhydrous CuCl$_2$ in tetrahydrofuran (40 ml). After stirring at –20 °C for 2 h the suspension was warmed to room temperature and stirred for another 16 h. The mixture was concentrated and dioxan–benzene (10 : 100 ml) added. The resulting suspension was stirred at 80 °C for 10 h. Removal of the copper by extraction with NH$_4$OH followed by concentration of the organic layer afforded 7,8-dihydrodibenzo-[*f,h*][1,4]dioxecin (I) (85%). Recrystallization of the crude product from pentane gave colourless plates, m.p. 99—100 °C (Found: C, 79.7; H, 6.6; O, 13.2. Calc. for C$_{16}$H$_{16}$O$_2$: C, 79.97; H, 6.71; O, 13.32%).

7,8-Dihydro-6,9-dimethyldibenzo[*f,h*][1,4]diazecin (II) was obtained similarly as an oil (92%). N.m.r. and mass spectral data are summarized in Table 1.

^{1}H *N.m.r. Spectroscopy*.—^{1}H n.m.r. spectra were recorded on a Varian HA 100 spectrometer. The AA'BB' part of the spectrum was obtained at 100 and 250 Hz sweepwidth, and line frequencies measured with a frequency counter.

On the basis of agreement between simulated and measured spectra a set of spin–spin coupling constants J_{AB}, $J_{AB'}$, $J_{AA'}$, and $J_{BB'}$ (SIMEQ program of II 16/3, see ref. 5) was found.

Crystal Structure and Molecular Geometry of (I).—*Crystal data*. C$_{16}$H$_{16}$O$_2$, $M = 240.3$, Orthorhombic, $a = 11.871(1)$, $b = 13.882(2)$, $c = 7.875(2)$ Å, $Z = 4$, $U = 1\,298$ Å^3, $F(000) = 512$. Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) = 6.4 cm^{-1}. Space group *Aba*2 from systematic ab-

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[1] (*a*) M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11; (*b*) R. J. Abraham and G. Gatti, *J. Chem. Soc.* (*B*), 1969, 961; (*c*) T. P. Forrest, *Org. Magnetic Resonance*, 1974, **6**, 355; (*d*) L. G. Vorontsova and A. F. Bochkov, *ibid.*, p. 654; (*e*) G. K. R. Pachler, *J.C.S. Perkin II*, 1972, 1936; (*f*) R. A. Austin and C. P. Lillya, *J. Org. Chem.*, 1969, **34**, 1327.

[2] P. L. Durette and D. Horton, *Org. Magnetic Resonance*, 1971, **3**, 417; L. G. Vorontsova and A. F. Bochkov, *ibid.*, 1975, **7**, 313; A. Fisher, E. Oppenheimer, and S. Cohen, *Tetrahedron*, 1975, **31**, 317.

[3] G. van Koten and J. G. Noltes, *J. Organometallic Chem.*, in the press.

[4] G. Bähr and F. W. Küpper, *Chem. Ber.*, 1967, **100**, 3992.

[5] C. W. F. Kort and M. J. A. de Bie, personal communication.

sences: *hkl* with $k + l$ odd, $0kl$ with k and l odd, $h0l$ with h odd.

TABLE 1

N.m.r. and mass spectroscopic data for (I) and (II)

Compound	δ/p.p.m.[a] NMe	δ/p.p.m.[a] $-XCH_2CH_2X-$	δ/p.p.m.[a] $PhCH_2X-$	δ/p.p.m.[a] Arom. H	Mass spectra[b] (m/e)
(I; X = –O–)		3.33m, 3.54m[c]	4.24d, 4.57d J_{gem} 12 Hz	6.9—7.6m	240 (P), 195, 179,* 165, 152, 139, 128, 115
(II; X = >NMe)	2.30s	2.14m, 2.71m[c]	3.11d, 3.70d J_{gem} 12 Hz	6.9—7.5m	266 (P), 251 (P–Me), 222 ($P-NC_2H_6$), 208, 194, 180, 179,* 165

[a] Tetramethylsilane as internal standard; room temperature; in CCl_4. [b] Some very abundant ions are mentioned; asterisk indicates base peak in spectrum. [c] Coupling constants are in Table 4.

Intensity data collection. A suitable specimen was mounted on an Enraf–Nonius CAD 4 diffractometer and X-ray intensity data were measured by use of Cu-K_α radiation. Accurate unit-cell parameters and the orientation matrix were determined from a least-squares treatment of the angular settings of 15 reflections. The standard deviations in the lattice parameters were obtained from the comparison of the deviations from integer values of the indices, calculated with the orientation reflections as described by Duisenberg.[6] Intensity data were collected for a redundant set of 861 reflections to $\theta_{max.}$ 55°. A standard reflection was measured every twenty-five reflections. A smooth function through these measurement values has been used to correct for fluctuations in the intensity data (2%). Averaging of equivalent data resulted in a set of 410 significant reflections with $I > 2.5\sigma(I)$. Intensities were corrected for Lorentz and polarization effects.

TABLE 2

Final refined co-ordinates for the non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
O(1)	0.395 2(2)	0.559 1(2)	−0.157 3(—)
C(1)	0.469 9(3)	0.453 2(2)	0.156 2(6)
C(2)	0.371 7(3)	0.437 4(3)	0.064 7(6)
C(3)	0.319 1(3)	0.346 7(3)	0.074 6(7)
C(4)	0.361 3(4)	0.275 5(3)	0.175 5(7)
C(5)	0.458 9(4)	0.290 6(3)	0.265 6(8)
C(6)	0.513 2(4)	0.376 4(3)	0.254 6(7)
C(7)	0.319 3(3)	0.513 7(3)	−0.043 4(8)
C(8)	0.438 0(4)	0.499 4(5)	−0.288 8(7)

Structure determination and refinement. The data were converted to normalized structure magnitudes and the structure solved by direct methods by use of the program MULTAN.[7] A Fourier synthesis calculated for the most probable solution gave the positions of all non-hydrogen atoms. Least-squares refinement of positional and isotropic temperature factors resulted in R 0.098. Continued refinement with anisotropic temperature factors reduced R to 0.078. Hydrogen atoms were located in a difference-Fourier synthesis. Subsequent refinement, including positional and isotropic parameters for the hydrogen atoms resulted in R 0.036. At this point the weighting scheme was changed from $w = 1$ in $w = 1/[\sigma^2(F_o) + 0.018F_o + 0.001F_o^2]$, so that the average $w(\Delta F)^2$ is about the same for similar-sized groups analysed in a systematic way, in ranges of F_o and $\sin(\theta)$. Full-matrix least-squares refinement converged to R 0.033 (R' 0.047). The average deviation in an observation of unit weight, defined by $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{\frac{1}{2}}$ was 1.02. A final difference-Fourier synthesis had no peaks >0.1 e Å^{-3}. At the end of refinement all parameter shifts were $<0.1\sigma$. All crystallographic calculations were performed with a version of the

TABLE 3

Final refined co-ordinates and thermal parameters for the hydrogen atoms, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	B/Å^2
H[C(3)]	0.256(4)	0.335(2)	0.009(5)	3(1)
H[C(4)]	0.327(3)	0.203(3)	0.172(5)	5(1)
H[C(5)]	0.492(5)	0.225(4)	0.325(9)	10(2)
H[C(6)]	0.585(3)	0.379(3)	0.309(6)	5(1)
H′[C(7)]	0.254(4)	0.487(3)	−0.113(6)	5(1)
H″[C(7)]	0.295(3)	0.560(3)	0.019(6)	5(1)
H′[C(8)]	0.409(4)	0.517(3)	−0.404(7)	5(1)
H″[C(8)]	0.412(4)	0.446(4)	−0.285(9)	7(2)

TABLE 4

^1H n.m.r. data for the $X{\cdot}CH_2{\cdot}CH_2{\cdot}X$ part of the ring in compounds (I) and (II)

	Solvent	Temp./°C	$\Delta\nu$[a]/Hz	Geminal J_{AB}/Hz	Vicinal[b] $J_{AA'}$	$J_{AB'}$	$J_{BB'}$
(I)	C_6D_6	*c*	29.24	−12.90	7.88	2.13	4.87
		107.4	24.21	−12.73	7.16	2.21	5.36
	CS_2	−15	20.93	−12.86	8.00	2.15	4.74
		c	20.27	−12.76	7.64	2.19	4.90
	CCl_4	*c*	22.25	−12.93	7.75	2.10	5.04
		78.0	21.11	−12.69	7.40	2.16	5.20
	[$^2H_8$]Toluene	−20	36.43	−12.82	8.31	2.08	4.38
(II)	C_6D_6	*c*	57.60	−14.35	8.49	5.51	4.30

[a] Shift difference (Hz) between protons A and B. [b] According to the notation used in ref. 16 $J_{AB'} = J_{A'B}$ correlate with J_g^g; $J_{AA'}$ with J_g^t and $J_{BB'}$ with $J_g^{g'}$. [c] Ambient.

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[6] A. J. M. Duisenberg, Collected Abstracts 1st European Enraf–Nonius CAD 4 Users Meeting, Paris, 1974.

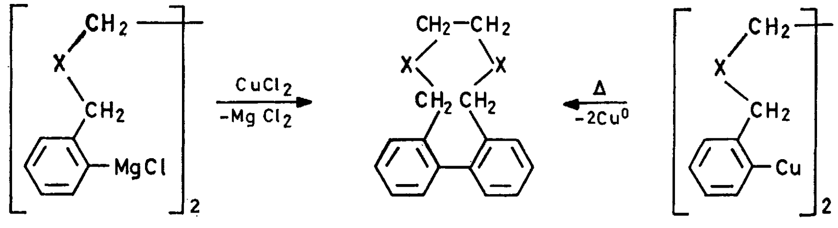
[7] 'X-Ray Program System. Technical Report TR 192, Computer Science Center, University of Maryland, implemented and extended by the Dutch X-Ray System Group, 1973.

X-Ray System,[7] which includes MULTAN. Final positional parameters of carbon and oxygen atoms are listed in Table 2. Final atomic co-ordinates and isotropic thermal parameters of hydrogens atoms are listed in Table 3. Atomic scattering factors for carbon and oxygen were taken from ref. 8 and for hydrogen from ref. 9.

Observed and calculated structure factors as well as final anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22094 (5 pp., 1 microfiche).*

RESULTS

7,8-Dihydrodibenzo[*f,h*][1,4]dioxecin (I) has been prepared in two ways: (i) from the interaction of 1,2-bis-[2-(bromomagnesio)benzyloxy]ethane with $CuCl_2$, and (ii) from the intramolecular ring-closure reaction of a tetranuclear organocopper compound: [3]



(I; X = —O—)
(II; X = >NMe*)

* In view of the strong resemblance of the molecular geometries of (I) and (II) the n.m.r. and mass spectroscopic data for (II) will not be discussed in detail.

The identity of (I), which has been isolated as a colourless crystalline solid, was established both by mass spectrometry and n.m.r. spectroscopy.

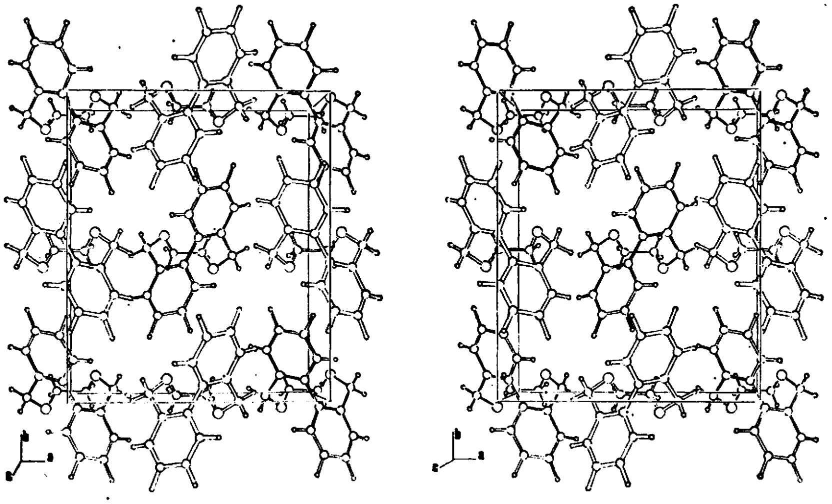


FIGURE 1 Stereoscopic view of the packing of the molecules in the crystal as viewed down the *c* axis

The mass spectra of (I) (see Table 1) showed the parent peak at *m/e* 240 whereas peaks at higher *m/e* values were absent. This indicates that intramolecular coupling had occurred and that the monomer with the ten-membered ring had been formed exclusively.

The n.m.r. spectrum of (I) (see Table 1) shows an AB pattern for the diastereotopic benzylic protons whereas the diastereotopic ethylenic protons are observed as an AA′BB′ pattern. Analysis of the latter part of the spectrum by routine methods gave a set of four coupling constants: three vicinal constants $^3J_{AA'}$, $^3J_{BB'}$, and $^3J_{AB'}$, and one geminal $^2J_{AB}$ (see later, Figure 4). This is fully compatible with a conformation for the ethylenic part of the molecule in which the oxygen atoms reside in *gauche* positions. N.m.r. data for compounds (I) and (II), recorded at different temperatures and for various solvents, are summarized in Table 4.

The crystal structure and molecular geometry of compound (I) was solved by *X*-ray techniques. The unit cell contains four discrete molecular units which are situated on the crystallographic two-fold axis. Figure 1 illustrates the packing of the molecules in the crystal [10] as viewed down the *c* axis. Since linking of two *ortho*-sites in biphenyl gives rise to a chiral molecule, (I) can exist in two optical isomeric forms. Both are present in the unit cell.

The ORTEP drawing [11] (Figure 2) clearly shows the ten-

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1976, Index issue.

[8] D. T. Cromer and J. H. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[9] R. F. Stewart, E. Davidson, and W. Simpson, *J. Phys. Chem.*, 1965, **42**, 3175.

[10] D. Kaas, Algol Program for Stereoscopic Drawings, University of Utrecht, 1968.

[11] C. K. Johnson, ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustration, 1971, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

membered ring as well as the angle between the two phenyl rings. This angle, which is defined by the least-squares plane through the six atoms of one phenyl ring and the plane through the symmetry-related ring, is 78.1°, a value comparable to those for other 2,2′-disubstituted methylbiphenyl compounds; these are in the range 71—86°.[12]

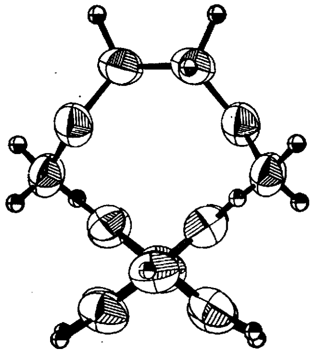

FIGURE 2 Geometry of the ten-membered ring system and the angle between the two phenyl rings

Figure 3 shows the atom labelling system and bond distances. The C(1)–C(1′) bond between the two phenyl groups [1.483(5) Å] is slightly shorter than that found in the crystal structure of biphenyl (1.51 Å) [12] where the phenyl groups are coplanar. However, it does not deviate significantly from the mean C–C value (1.52 Å) [13] for other *ortho*-disubstituted biphenyl derivatives.

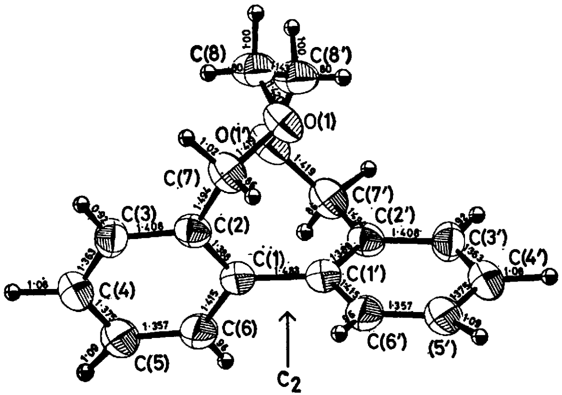

FIGURE 3 Labelling of the atoms and bond distances; standard deviations are 0.005—0.007 Å for distances not involving H atoms, and 0.04—0.06 for those involving H

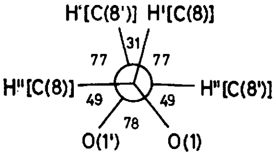

FIGURE 4 Newman projection along the C(8) ··· C(8′) axis showing the dihedral bond angles: $J_g^g = {}^3J$(H′[C(8)] ··· H″[C(8′)]) = ${}^3J$(H′[C(8′)] ··· H″[C(8)]); $J_g^{g'} = {}^3J$(H′[C(8′)] ··· H′[C(8)]); and $J_g^t = {}^3J$(H″[C(8)] ··· H″[C(8′)])

The torsion angles (see Table 5) around the C(8)–C(8′) bond, which are important with respect to the conformation of the ·O·CH_2·CH_2·O· moiety, are shown in a Newman projection along this bond [14] (Figure 4). The conformation is approximately staggered with the oxygen atoms *gauche*. The H–C–C–H torsion angles deviate strongly from 60° (see Discussion section). There are no unusually short intramolecular distances (see Figure 3) or exceptional bond angles (see Table 6) for atoms in the ten-membered ring.

TABLE 5

Torsion angles (°)

	Angle
C(2)–C(1)–C(1′)–C(2′)	–104
C(2)–C(1)–C(1′)–C(6′)	77
C(6)–C(1)–C(1′)–C(6′)	–102
C(1′)–C(1)–C(2)–C(3)	–179
C(1′)–C(1)–C(2)–C(7)	1
C(6)–C(1)–C(2)–C(3)	1
C(6)–C(1)–C(2)–C(7)	180
C(1)–C(2)–C(7)–O(1)	50
C(3)–C(2)–C(7)–O(1)	–130
C(2)–C(7)–O(1)–C(8)	67
C(8′)–C(8)–O(1)–C(7)	–125
O(1)–C(8)–C(8′)–O(1′)	78
C(1)–C(2)–C(7)–H′[C(7)]	172
C(1)–C(2)–C(7)–H″[C(7)]	–66
C(3)–C(2)–C(7)–H′[C(7)]	–8
C(3)–C(2)–C(7)–H″[C(7)]	113
H′[C(7)]–C(7)–O(1)–C(8)	–58
H″[C(7)]–C(7)–O(1)–C(8)	–173
C(7)–O(1)–C(8)–H′[C(8)]	111
C(7)–O(1)–C(8)–H″[C(8)]	2
O(1)–C(8)–C(8′)–H′[C(8′)]	–157
O(1)–C(8)–C(8′)–H″[C(8′)]	–49
H′[C(8)]–C(8)–C(8′)–H′[C(8′)]	–31
H′[C(8)]–C(8)–C(8′)–H″[C(8′)]	77
H″[C(8)]–C(8)–C(8′)–H″[C(8′)]	–176

TABLE 6

Bond angles (°)

C(2)–C(1)–C(6)	118.1(3)	C(5)–C(4)–H[C(4)]	118(2)
C(1)–C(2)–C(3)	119.0(4)	C(4)–C(5)–H[C(5)]	113(3)
C(2)–C(3)–C(4)	121.1(4)	C(6)–C(5)–H[C(5)]	126(3)
C(3)–C(4)–C(5)	120.1(4)	C(5)–C(6)–H[C(6)]	115(2)
C(4)–C(5)–C(6)	120.0(4)	C(1)–C(6)–H[C(6)]	122(2)
C(5)–C(6)–C(1)	121.6(4)	C(2)–C(7)–H′[C(7)]	112(2)
C(1′)–C(1)–C(6)	119.0(4)	C(2)–C(7)–H″[C(7)]	110(3)
C(1′)–C(1)–C(2)	122.9(4)	O(1)–C(7)–H′[C(7)]	107(3)
C(1)–C(2)–C(7)	122.3(4)	O(1)–C(7)–H″[C(7)]	104(3)
C(3)–C(2)–C(7)	118.7(4)	H′[C(7)]–C(7)–H″[C(7)]	109(4)
C(2)–C(7)–O(1)	114.2(3)	O(1)–C(8)–H′[C(8)]	113(3)
O(1)–C(8)–C(8′)	110.5(4)	O(1)–C(8)–H″[C(8)]	112(5)
C(7)–O(1)–C(8)	115.4(4)	C(8′)–C(8)–H′[C(8)]	110(3)
C(2)–C(3)–H[C(3)]	119(2)	C(8′)–C(8)–H″[C(8)]	114(4)
C(4)–C(3)–H[C(3)]	120(2)	H′[C(8)]–C(8)–H″[C(8)]	97(6)
C(3)–C(4)–H[C(4)]	121(2)		

DISCUSSION

The first ${}^3J_{HH'}/\phi$ correlation equation was suggested by Karplus [1a] on the basis of theoretical considerations. Modifications of this equation have been made on the basis of detailed studies of the trend of ${}^3J_{HH'}$ values in a series of 1,2-disubstituted derivatives.[1b-f] These equations which are now employed for the calculation of dihedral angles, ϕ, from ${}^3J_{HH'}$ values, differ with respect to the weight given to each of the following molecular

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[12] R. W. G. Wyckoff, Crystal Structures, 2nd edn., Vol. 6, Wiley, New York, 1971, pp. 1—17.

[13] *Chem. Soc. Special Publ.*, No. 18, 1965.

[14] N. P. Brandenburg, A Fortran Program for Newman Plots, 1972, University of Amsterdam.

parameters, the electronegativity of the substituents as well as the angle they make with the coupled proton, rotamer populations, and bond lengths.

Recently, Abraham and Gatti[1b] established a linear correlation between vicinal coupling constants and the electronegativity (E_X) of the substituents X in $XCH_2{\cdot}CH_2X$ compounds. The correlation equations which were derived for the *gauche* conformations are:

$$J_g^g = 8.94 - 0.94\,(\Sigma E_X) \qquad (1a)$$

$$J_g^t + J_g^{g'} = 26.92 - 2.03\,(\Sigma E_X) \qquad (1b)$$

in which ΣE_X is 7.0 for compound (I) and 6.1 for (II). Substitution of these ΣE_X values in equations (1*a*) and (1*b*) gives J_g^g and $J_g^t + J_g^{g'}$ values * which for compound (I) appear to be in excellent agreement with the measured coupling constants (see Table 7). In contrast, calculation of $J_g^{g'}$ from the equation:

$$J_g^{g'} = 10.45 - 1.43\,(\Sigma E_X) \qquad (2)$$

affords values which differ considerably from the measured vicinal coupling constants.[15]

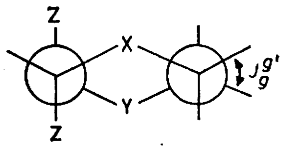
TABLE 7

Comparison of measured and calculated vicinal coupling constants ${}^3J$

	Obs.			Calc.[a,b]	
	CCl_4	C_6D_6	CS_2		
Cpd (I) (ΣE_O 7.0)[c]					
J_g^t	7.75	7.88	7.64		12.27
$J_g^{g'}$	5.04	4.87	4.90	0.92	0.44
$J_g^t + J_g^{g'}$	12.79	12.75	12.54		12.71
J_g^g	2.10	2.13	2.19	2.29	2.36
Cpd (II) (ΣE_N 6.1)[c]					
J_g^t		8.49			12.81
$J_g^{g'}$		4.30		1.91	1.73
$J_g^t + J_g^{g'}$		12.79			14.54
J_g^g		5.51		3.14	3.21

[a] Left-hand col., see ref. 1*c*. [b] Right-hand col., see ref. 1*b*. [c] According to electronegativities used in ref. 1(*b*) (Table 4).

A possible explanation would seem the fact that equations (1*a*) and (1*b*) have been derived by Abraham and Gatti from measurements of a series of compounds which have staggered equilibrium conformations, *i.e.* $\phi \approx 60°$. Also the $J_g^{g'}$ correlation equation has been obtained from low-temperature n.m.r. measurements of six-membered ring compounds (III)—(V),[1b] which are known to exist in the classical chair conformation (*i.e.* ϕ 60°) below the temperature of 'conformational freeze-out.' Accordingly, the use of these equations would seem to be restricted for the calculation of ${}^3J_{HH}$ values in compounds which have ϕ angles equal or very close to 60°. This conclusion is supported by the excellent agreement between the measured and calculated $J_g^{g'}$ value of [2,2]metacyclophane.[16] The $CH_2{\cdot}CH_2$ groups in this compound, which was not included by Gatti and Abraham in their study, are locked in a symmetrical staggered conformation (ϕ 60°). Furthermore, the orientation-dependent correlation between E_X and ${}^3J_{g'}$, which recently has been formulated by Forrest[1c] on the basis of a series of $XCH_2{\cdot}CH_2X$ compounds containing ϕ equal to 60°, gives values for J_g^g and $J_g^{g'}$ which likewise are not in accord with the measured values (Table 7).



(III) X = Y = > CD_2; Z = H
(IV) X = Y = –O–; Z = Me
(V) X = –O–; Y = >NH; Z = H

In an attempt to determine the degree of deviation from the symmetrical staggered conformation the ${}^3J/\phi$ correlation equation, which has been established by Vorontsova and Bochkov,[1d] has been applied. These authors obtained equation (3) by an experimental correlation of ${}^3J_{HH'}$ values and bond angles ranging from 18 to 100° in two conformationally rigid heteroisoadamantane derivatives:

$$ {}^3J_{HH'} = (4.37 + 4.39\cos\psi + 3.32\cos 2\psi)(1.28 - 0.041\,Y) \qquad (3)$$

where ψ represents the angle between the directions of the vicinal H–C bonds, and Y is the sum of the chemical shifts (δ p.p.m.).

The results for compound (I), summarized in Table 8, prompted us to determine the molecular geometry of the solid in order to establish the actual dihedral bond angles ϕ and ψ, and to ensure that the molecule was free from any serious distortions.

TABLE 8

Application of ${}^3J_{HH'}/\psi$ correlation equation

		Found		Calc.
	Y[a]/p.p.m.	J_g/Hz	ψ[b]/°	ψ/°
J_g^g	6.86	2.10	86 (6)	79
$J_g^{g'}$	6.86	7.75	50 (4)	43.3
	6.64			

[a] Sum of chemical shifts of A and B on the δ scale. Since it is not known which δ position belongs to A or to B both sums are used for the calculation of the C(8)–H′[C(8)] ··· C(8′)–H′[C(8′)] angle. [b] From crystal data.

In general, the values of ϕ and likewise those of ψ in $XCH_2{\cdot}CH_2X$ systems are determined by the interplay of rotational changes about the various bonds, by changes in the C–C–X bond angles, and by repulsive forces between the X substituents. For (I) conformational changes are restricted as a result of the presence of the biphenyl system with sp^2 hybridized carbon atoms, the blocked rotation about the C(1)–C(1′)

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* Figure 4 illustrates how the different notations which are used for the vicinal coupling constants correlate.

[15] J. B. Lambert, *J. Amer. Chem. Soc.*, 1967, **89**, 1836; J. B. Lambert, R. G. Keske, and D. K. Weary, *ibid.*, p. 5921; R. J. Abraham and W. A. Thomas, *Chem. Comm.*, 1965, 431.

[16] H. S. Gutowsky and C. Juan, *Disc. Faraday Soc.*, 1962, **34**, 52.

bond, and the fact that the *ortho*-sites of the molecule are linked.

The molecular geometry of (I) obtained from the *X*-ray study shows that the *gauche* conformation for the $OCH_2{\cdot}CH_2O$ bridge is likewise present in the solid. The absence of any unusual bond distances or angles in the molecule indicates that the observed molecular geometry is free of conformational strain. In view of both these results and the constraints of the ten-membered ring in (I) it is plausible to assume that the observed conformation for the $OCH_2{\cdot}CH_2O$ bridge in the solid strongly resembles the equilibrium conformation in solution. This line of reasoning was also successful in the case of [2,2]metacyclophane [ϕ(solid) 59° *vs.* ϕ(solution) 60°].[16,17]

The Newman projection (Figure 4) shows that the dihedral angle between the oxygen atoms has opened to 78° and represents an adjustment by the molecule to reduce the repulsive interactions between these atoms. This results in dihedral angles between the hydrogen atoms which deviate considerably from 60°. Comparison of the ψ-values (Table 8) then reveals that equation (3) successfully predicts the magnitude of the deviation from the idealized value of 60° for the *gauche*-oriented proton pairs in solution.

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[17] C. J. Brown, *J. Chem. Soc.*, 1953, 3278.