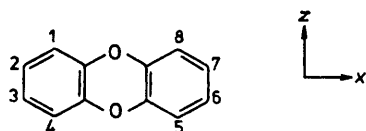


## Conformational Investigation of Dibenzo-*p*-dioxin by Proton Magnetic Resonance in a Liquid Crystalline Solvent

By Giovanni Fronza \* and Enzo Ragg, Istituto di Chimica del Politecnico, Centro del CNR per la Chimica delle Sostanze Organiche Naturali, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

The structure of dibenzo-*p*-dioxin has been studied by the nematic liquid crystal n.m.r. method. This molecule in solution adopts a folded conformation about the axis connecting the two heteroatoms with an angle of folding of  $165.6 \pm 2^\circ$ .

THE molecule of dibenzo-*p*-dioxin (1) was extensively studied both in solution and in the solid state to determine the angle of folding,  $\phi$ . This angle is defined as the dihedral angle between the two aromatic rings. Three reports<sup>1-3</sup> have appeared on the X-ray analysis of dibenzo-*p*-dioxin, all concluding that the molecule is planar within experimental error, although the possibility of a disordered structure with slightly folded molecules might not be excluded in view of the remarkable diffuse scatterings obtained with such a crystal.



(1)

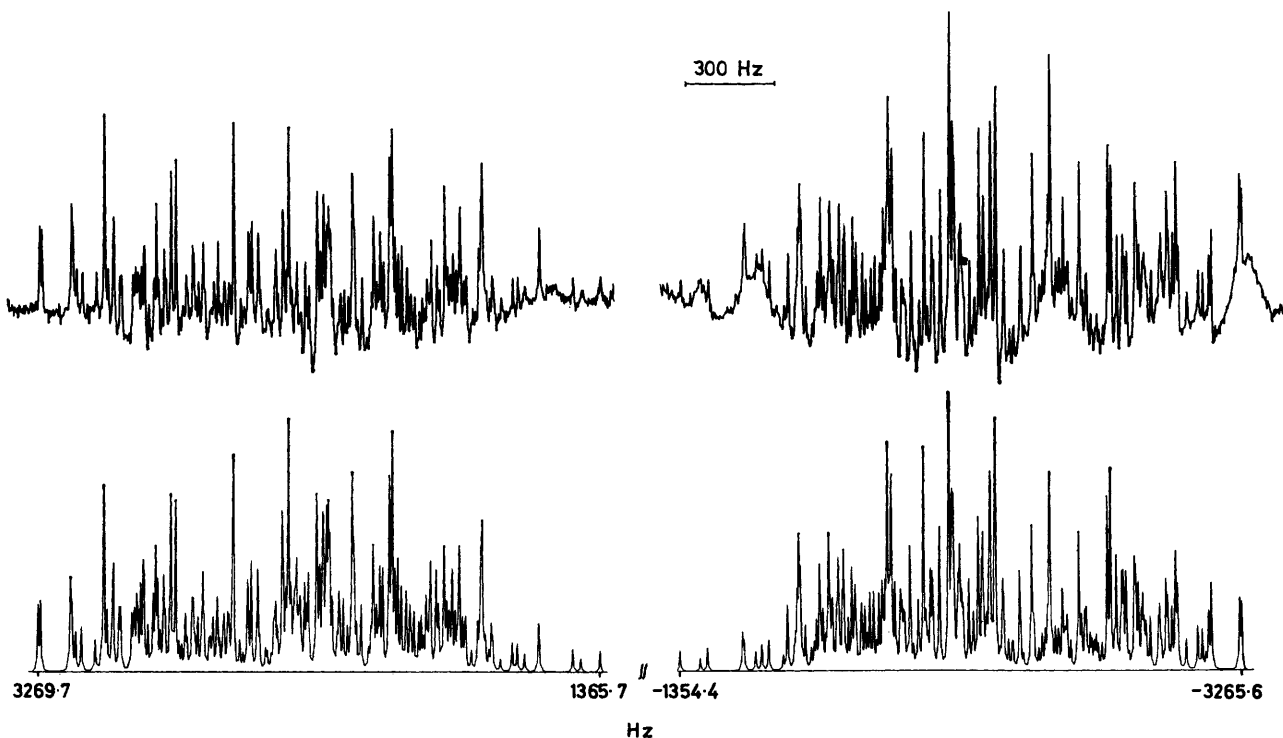
On the other hand spectroscopic studies in solution indicate that this molecule is folded along the axis connecting the two heteroatoms. From the analysis of dipole moment data for dibenzo-*p*-dioxin in benzene Pappalardo *et al.*<sup>4</sup> obtained an angle of folding of  $163.8^\circ$ . The folded conformation of (1) in solution is also sup-

ported from the dielectric relaxation studies in dilute solution in benzene by Koga *et al.*<sup>5</sup> and from the dielectric polarization studies by Davies and Swain.<sup>6</sup> These latter authors have found a dielectric absorption due to the butterfly-flapping motion for (1) dissolved in a polystyrene matrix. In addition, the u.v.<sup>4,7</sup> and the photoelectron<sup>4</sup> spectroscopic data also indicate a folded conformation for dibenzo-*p*-dioxin.

N.m.r. spectroscopy of compounds partially oriented in a nematic phase is in principle a powerful method for the determination of molecular geometries in the liquid phase.<sup>8,9</sup> Khetrpal<sup>10</sup> has recently extended this method to the relatively large tricyclic systems in a study of the planar molecule phenazine. In this study we have investigated dibenzo-*p*-dioxin in order to obtain the angle of folding in solution in an orienting medium.

### EXPERIMENTAL

The n.m.r. spectrum of (1) was recorded with a Varian XL-100-15 spectrometer at the probe temperature ( $35^\circ\text{C}$ ). A 5 mole % solution of dibenzo-*p*-dioxin was prepared in 4-*n*-butyl-4'-methoxyazoxybenzene (Licristal Merck Phase IV); the position of 230 lines (Figure) could be determined experimentally with a width at half-height of 4 Hz.



Experimental (top) and simulated (bottom)  $^1\text{H}$  n.m.r. spectrum of dibenzo-*p*-dioxin partially oriented in the nematic phase of 4-*n*-butyl-4'-methoxyazoxybenzene (Merck Licristal Phase IV)

The spectra were analyzed with the LACXLC iterative program on a UNIVAC 1100/80 computer. The indirect coupling constants  $J_{ij}$  were taken<sup>11</sup> from the isotropic spectrum in  $\text{CDCl}_3$  and were kept constant,  $J_{12}$  8.2,  $J_{13}$  1.5,  $J_{14}$  0.5 Hz. All the inter-ring coupling constants were assumed to be zero. The observed root mean square error between the experimental and calculated line positions was 0.7 Hz with a maximum deviation of 2.0 Hz. The calculated and experimental spectra of dibenzo-*p*-dioxin are reported in the Figure.

#### RESULTS AND DISCUSSION

The oriented spectrum of dibenzo-*p*-dioxin has been interpreted in terms of ten dipolar couplings and two chemical shifts, confirming  $D_{2h}$  symmetry for the planar molecule or  $C_{2v}$  symmetry for two rapidly interconverting bent structures. The energy barrier of the ring-inversion process has been estimated from the dielectric relaxation<sup>5</sup> and dielectric polarization<sup>6</sup> studies and was found to be very near to zero ( $0.0005 \text{ kcal mol}^{-1}$ ). Such a low

distances and the two orientational parameters. Thus the system is largely overdetermined since ten different dipolar couplings are available.

The geometrical calculations have been performed using the program SHAPE<sup>12</sup> and the results are given in the Table along with the experimental parameters. The ratio between the interproton distances  $r_{14}$  and  $r_{23}$  can be obtained directly from the ratio of the dipolar couplings  $D_{23}$  and  $D_{14}$ . These distances were kept constant in the 'least-squares-fit' program SHAPE. The calculations were done for the rigid planar and for the bent structures and the deviations between the calculated and experimental  $D_{ij}$  values are reported in the Table. An inspection of the Table shows that the deviations for the inter-ring  $D_{ij}$  values are much larger for the planar than for the bent conformation, clearly indicating that the molecule is puckered. On the other hand, the values of the dipolar couplings between protons located on a single aromatic ring are re-

Experimental and computed data of dibenzo-*p*-dioxin (1)<sup>a</sup>

Parameter (Hz)	Experimental value	$D_{\text{calc.}} - D_{\text{exp.}}$ (folded conformation)	$D_{\text{calc.}} - D_{\text{exp.}}$ (planar conformation)	Geometrical parameters <sup>b</sup>
$D_{12}$	$-1\ 559.16 \pm 0.03$	0.00	0.01	$r_{12}/r_{23} = 1.008 \pm 0.004$
$D_{13}$	$-52.43 \pm 0.04$	0.01	0.01	$r_{13}/r_{23} = 1.741 \pm 0.002$
$D_{14}$	$48.01 \pm 0.13$	0.00	0.00	$r_{14}/r_{23} = 2.013 \pm 0.002$
$D_{15}$	$-42.35 \pm 0.13$	-0.22	-1.70	$r_{15}/r_{23} = 2.759 \pm 0.003$
$D_{16}$	$-55.15 \pm 0.04$	-0.05	-0.94	$r_{16}/r_{23} = 3.139 \pm 0.001$
$D_{17}$	$-102.15 \pm 0.04$	-0.01	-0.82	$r_{17}/r_{23} = 2.799 \pm 0.009$
$D_{18}$	$-348.37 \pm 0.13$	-0.02	2.34	$r_{18}/r_{23} = 1.886 \pm 0.001$
$D_{23}$	$391.68 \pm 0.13$	0.01	-0.01	$r_{26}/r_{23} = 3.752 \pm 0.001$
$D_{26}$	$-40.29 \pm 0.13$	0.30	-0.63	$r_{27}/r_{23} = 3.617 \pm 0.02$
$D_{27}$	$-48.99 \pm 0.13$	0.43	-0.64	
$\nu_1 - \nu_8$ (Hz)	$26.1 \pm 0.25$			$\phi = 165.6 \pm 2^\circ$
wtrms (Hz)		0.072	0.655 5	
$S_{xx}$		0.297 41	0.288 89	
		$\pm 0.000 18$	$\pm 0.000 15$	
$S_{zz}$		-0.049 82	-0.049 82	
		$\pm 0.000 01$	$\pm 0.000 01$	

<sup>a</sup> The indirect coupling constants were assumed according to ref. 11 (see Experimental section). <sup>b</sup>  $r_{23} = 2.481 \text{ \AA}$  (assumed).

barrier to ring planarity suggests that a dynamic averaging over a number of states with different geometries occurs rather than a static averaging over only two rigid bent structures. If the potential function for ring puckering is known, the averaging over a number of non-planar vibrational levels can be included in the calculation. However the application of this method is restricted to those molecules for which the potential function is available.

To our knowledge the potential function for dibenzo-*p*-dioxin is not known; we have used an approximate approach assuming that the non-planar molecule rapidly interconverts only between two rigid bent conformers. Since the two conformers in equilibrium are characterized by the same orientational parameters and the same interproton distances, the problem of averaging over structures with opposite conformations could be avoided and the calculations were performed as if the molecule existed in a single rigid bent conformation. The bent molecule has  $C_{2v}$  symmetry and requires six direct couplings to describe the four independent interproton

produced with a comparable accuracy in the two structures, as expected, since the butterfly-flapping motion must affect only the inter-ring proton distances. However several inter-ring  $D_{ij}$  values show deviations, even in the 'best-fit' bent structure, which still exceed the experimental error. This is not surprising in view of the assumption that the molecule interconverts only between two rigid bent conformers and reflects the fact that there is probably a broad conformational distribution around the potential minimum.

The angle of folding, although approximated by the limitations of this approach, can be calculated through equation (1). A value of  $165.6^\circ$  was obtained, in

$$\phi = 180 - 2 \arctan(y_2 - y_1)/(x_2 - x_1) \quad (1)$$

excellent agreement with the angle determined from the dipole moment data<sup>4</sup> ( $163.8^\circ$ ). The standard deviation of  $\phi$ , derived from the standard deviations of the proton co-ordinates, is  $\pm 0.2^\circ$ . This value is certainly too small. Further calculations showed that the deviations between the calculated and experimental  $D_{ij}$  values do

not vary appreciably by changing the angle of folding within  $\pm 2^\circ$ . Therefore a reasonable estimate of the error in the angle of folding determined with this method is  $\pm 2^\circ$ .

The ratios of the interproton distances are reported in the Table. The comparison with phenazine<sup>10</sup> shows that the inter-ring distances are slightly smaller in dibenzo-*p*-dioxin ( $r_{18}/r_{23} = 1.886$ ) than in phenazine ( $r_{18}/r_{23} = 1.937$ ). The distance ratios between protons located on a single aromatic ring are in reasonable agreement in the two molecules. Finally the elements of the ordering matrix  $S_{xx}$  and  $S_{zz}$  for (1) (Table) are in line with those of phenazine according to the very similar molecular shapes of the two molecules.

We thank Dr. J. W. Emsley for helpful discussions and Dr. G. F. Bettinetti for providing the sample.

[1/1317 Received, 17th August, 1981]

## REFERENCES

- <sup>1</sup> M. Senna, Z. Taira, T. Taga, and K. Osaki, *Cryst. Struct. Commun.*, 1973, **2**, 311.
- <sup>2</sup> A. W. Cordes and C. K. Fair, *Acta Crystallogr.*, 1974, **B30**, 1621.
- <sup>3</sup> P. Singh and J. D. McKinney, *Acta Crystallogr.*, 1978, **B34**, 2956.
- <sup>4</sup> F. P. Colonna, G. Distefano, V. Galasso, K. J. Irgolic, C. E. King, and G. C. Pappalardo, *J. Organomet. Chem.*, 1978, **146**, 235 and references cited therein.
- <sup>5</sup> Y. Koga, H. Takahashi, and K. Higasi, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 3359.
- <sup>6</sup> M. Davies and J. Swain, *Trans. Faraday Soc.*, 1971, **67**, 1637.
- <sup>7</sup> M. Kamiya, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1589.
- <sup>8</sup> J. W. Emsley and J. C. Lindon, 'NMR Spectroscopy Using Liquid Crystal Solvents,' Pergamon, Oxford, 1975.
- <sup>9</sup> L. Lunazzi, in 'Determination of Organic Structures by Physical Methods,' eds. F. C. Nachod and J. J. Zuckermann, Academic Press, New York, vol. **6**, 1976.
- <sup>10</sup> C. L. Khetrapal, *Org. Magn. Reson.*, 1981, **15**, 238.
- <sup>11</sup> N. E. Sharpless, R. B. Bradley, and J. A. Ferretti, *Org. Magn. Reson.*, 1974, **6**, 115.
- <sup>12</sup> P. Diehl, H. P. Kellerhals, and W. Niederberger, *J. Magn. Reson.*, 1971, **4**, 352.