

# Atropisomerism in bisphenols: free jet absorption millimeter wave study of 2,2'-biphenol

Paolo Ottaviani, Assimo Maris, Walther Caminati\*

*Dipartimento di Chimica "G. Ciamician" dell'Università, Via Selmi 2, I-40126 Bologna, Italy*

Received 18 November 2003; revised 3 December 2003; accepted 8 December 2003

## Abstract

The rotational spectrum of 2,2'-biphenol has been investigated by millimeter wave absorption free jet spectroscopy. The two sides of the phenyl rings with attached the hydroxyl group form a dihedral angle of 112.7°. Each hydroxyl group is nearly co-planar to the ring to which it belongs, and points towards the  $\pi$  system of the adjacent ring.

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** Rotational spectroscopy; Hydrogen bond; Free jets; Chirality

## 1. Introduction

2,2'-Biphenol (2,2'-dihydroxybiphenyl, since now on, 2BP) is the simplest member of bisphenols, a family of compounds which appears to have antioxidant properties [1]. 2BP is drawn in Fig. 1, where atom numbering and definition of the valence angle  $\alpha$  and internal rotation dihedral angle  $\tau$  are also given. One can see from the schematic representation that the molecule does not have a plane of symmetry and that upon restricted rotation about the  $C_1-C_1'$  bond can generate the mirror image. This is a special kind of chirality, which generates equivalent isomers called *atropisomers* [2]. The barrier to the isomer interconversion is much lower than that of normal enantiomeric substances, so that the corresponding tunneling splittings could be observed within the high spectral resolution, which underlines pure rotational spectroscopy. Such a splitting was already measured by MW spectroscopy in the case of the atropisomerism generated by the internal rotation of the hydroxyl group in the gauche form of isopropanol [3].

Lucarini et al. studied recently a related compound, 3,3'-di-*tert*-butyl-5,5'-dimethyl(1,1'-biphenyl)-2,2'-diol [1]. From the red shift of the absorption band of the OH stretching

(found at  $3531\text{ cm}^{-1}$ ) in the FT-IR spectrum (recorded in diluted  $\text{CCl}_4$  solutions) they deduced the presence of an internal hydrogen bond. They also carried out semi-empirical AM1 calculations on 2BP and predicted that the two aromatic rings make a dihedral angle of 55° and the two hydroxyl groups are in a *cisoid* geometry. These calculations also gave a hydrogen–oxygen distance of 2.5 Å, which—they said—is in agreement with expectations for the formation of hydrogen bonding between the two OH groups. This distance appears too high, however, if compared to 1.9–2.0 Å for normal  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds [4].

No structural or spectroscopic investigations are available in the literature on 2BP. Its equilibrium conformation should be a compromise between the repulsive effects of the two adjacent oxygens, and the propensity of the two hydroxyl groups to form hydrogen bonds, either with the nearby oxygens and/or the benzene  $\pi$  systems.

Based on all the above considerations, we decided to investigate the prototype molecule of the family, 2BP, by pure rotational spectroscopy.

## 2. Experimental

2BP was purchased from Aldrich and used without further purification. The microwave measurements

\* Corresponding author. Tel.: +39-051-2099480; fax: +39-051-2099456.

E-mail address: [caminati@ciam.unibo.it](mailto:caminati@ciam.unibo.it) (W. Caminati).

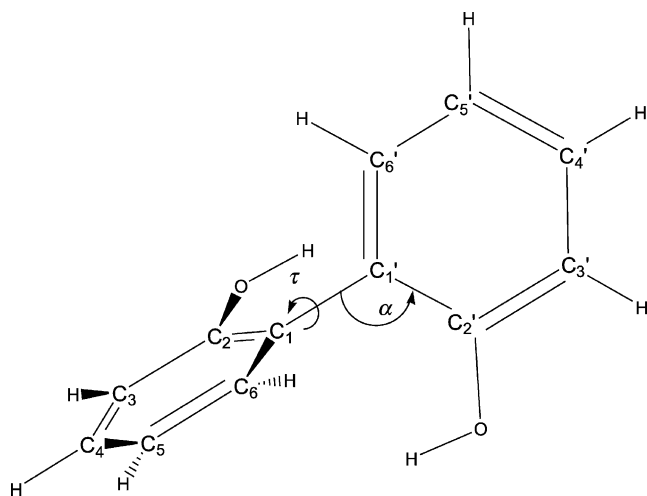


Fig. 1. Drawing of the 2BP, with atom numbering and definition of the valence angle  $\alpha$  and internal rotation dihedral angle  $\tau$ .

have been performed with a free jet spectrometer [5]. The relatively high melting (109 °C) and boiling (315 °C) points of 2BP, required the sample to be heated in order to have a sufficient vapor pressure. The best experimental conditions were obtained flowing argon at a stagnation pressure of ca. 30 kPa over 2BP at a temperature of ca. 165 °C, and expanding the mixture to about 50 mPa through a 0.35 mm diameter nozzle.

### 3. Results and discussion

#### 3.1. Assignment of the rotational spectrum

The rotational spectrum was assigned on the basis of the theoretical structure, obtained as described in Section 3.2. The strongest lines, corresponding to the lowest  $J$  transitions ( $J = 26$ –25) observable in our frequency range, were detected first. They have a  $S/N$  ratio of about 10/1 with time constant of 1 s. Weaker transitions up to  $J = 40$  have been then measured.  $K_a$  of the measured transitions was in the range 14–19, so that all measured transitions were doubly overlapped because of the asymmetry degeneracy of the involved levels. Such a systematic coalescence of lines does not allow to distinguish if the spectrum is a b- or a c-type spectrum.

The measured transitions are reported in Table 1. They have been fit with Watson Hamiltonian [6] (A reduction and I' representation). The centrifugal distortion is so small that, in spite of the quite high  $J$  and  $K_a$  available, only two ( $\Delta_J$  and  $\Delta_{JK}$ , very small values) of the five quartic centrifugal distortion constants have been determined.

The spectroscopic constants obtained are listed in Table 2 together with some statistical parameters of the fits.

According to the arguments given in the Section 3.2, we were not able to observe the spectrum of the O- $d_2$  species.

Table 1  
Measured frequencies of 2BP

$J'(K'_a) \leftarrow J''(K''_a)$	$\nu$ (MHz)	$J'(K'_a) \leftarrow J''(K''_a)$	$\nu$ (MHz)
26(19)–25(18)	60,145.36	34(17)–33(16)	63,602.76
27(19)–26(18)	61,067.52	34(18)–33(17)	65,560.97
28(18)–27(17)	60,034.61	34(19)–33(18)	67,518.03
28(19)–27(18)	61,989.58	35(15)–34(14)	60,597.47
29(18)–28(17)	60,956.25	35(16)–34(15)	62,561.27
29(19)–28(18)	62,911.40	35(17)–34(16)	64,522.17
30(17)–29(16)	59,921.66	35(18)–34(17)	66,481.08
30(18)–29(17)	61,877.75	35(19)–34(18)	68,438.59
30(19)–29(18)	63,833.19	36(15)–35(14)	61,513.72
31(17)–30(16)	60,842.37	36(16)–35(15)	63,479.06
31(18)–30(17)	62,798.88	36(17)–35(16)	65,441.11
31(19)–30(18)	64,754.68	36(19)–35(18)	69,358.92
32(16)–31(15)	59,804.66	37(14)–36(13)	60,456.51
32(17)–31(16)	61,762.88	37(15)–36(14)	62,429.16
32(18)–31(17)	63,719.92	37(16)–36(15)	64,396.17
32(19)–31(18)	65,676.07	37(17)–36(16)	66,359.53
33(16)–32(15)	60,724.10	38(14)–37(13)	61,368.43
33(17)–32(16)	62,683.02	38(15)–37(14)	63,343.77
33(18)–32(17)	64,640.66	38(16)–37(15)	65,312.73
33(19)–32(18)	66,597.14	39(16)–38(15)	66,228.52
34(16)–33(15)	61,642.86	40(16)–39(15)	67,143.53

All transitions are doubly overlapped due to the near prolate degeneracy of the involved levels: only  $K_a$  is given.

#### 3.2. Failure to observe the O- $d_2$ deuterated species of 2BP

In order to locate the position of the two hydroxyl hydrogens, we planned to investigate the O- $d_2$  isotopomer. It is easy, indeed, to obtain the deuterations of the hydroxyl groups, just shaking the compound with D<sub>2</sub>O. Unfortunately, in spite of several trials, we were not able to observe the rotational spectrum of this isotopomer. We realized that we already met this difficulty in observing the rotational spectra of partially deuterated species of aromatic hydroxides. For example we could not observe the deuterated species of resorcinol [7]. Similar problems have been met in other laboratories. Nosenko et al., when performing supersonic jet experiments on pyridylindoles [8,9], found that when heating these samples to temperatures higher than ca. 100 °C, a redistribution of deuterium atoms takes place with the aromatic ring hydrogens. Some more literature is available on this argument [10,11].

Table 2  
Spectroscopic constants of 2BP

A (MHz)	1438.635(4)
B (MHz)	491.559(17)
C (MHz)	430.365(21)
$\Delta_J$ (Hz)	19(2)
$\Delta_{JK}$ (Hz)	86(5)
N	42
$\sigma$ (MHz)	0.04

N and  $\sigma$  are the number of transitions and the standard deviation of the fit, respectively.

Table 3  
Calculated structure (B3LYP/6-311++G\*\*\*) of 2BP

Bond distances (Å)		Valence angles (°)	
C <sub>1</sub> –C <sub>1'</sub>	1.4939	C <sub>1</sub> –C <sub>1'</sub> –C <sub>2'</sub>	120.2
C <sub>2</sub> –C <sub>1</sub>	1.4080	C <sub>2</sub> –C <sub>1</sub> –C <sub>6</sub>	118.2
C <sub>3</sub> –C <sub>2</sub>	1.3966	C <sub>3</sub> –C <sub>2</sub> –C <sub>1</sub>	120.6
C <sub>4</sub> –C <sub>3</sub>	1.3897	C <sub>4</sub> –C <sub>3</sub> –C <sub>2</sub>	120.0
C <sub>5</sub> –C <sub>4</sub>	1.3956	C <sub>5</sub> –C <sub>4</sub> –C <sub>3</sub>	120.5
C <sub>6</sub> –C <sub>1</sub>	1.4029	C <sub>1</sub> –C <sub>6</sub> –C <sub>5</sub>	121.4
C–O	1.3631	O–C <sub>2</sub> –C <sub>1</sub>	122.1
O–H	0.9670	H–O–C <sub>2</sub>	109.2

All dihedral angles are in the range  $(180 \pm 0.5)^\circ$ , except  $\tau(C_2C_1 - C_1' C_2') = 107^\circ$ . All C–H bond lengths and CCH angles are in the ranges 1.083–1.085 Å and  $120 \pm 1^\circ$ , respectively.

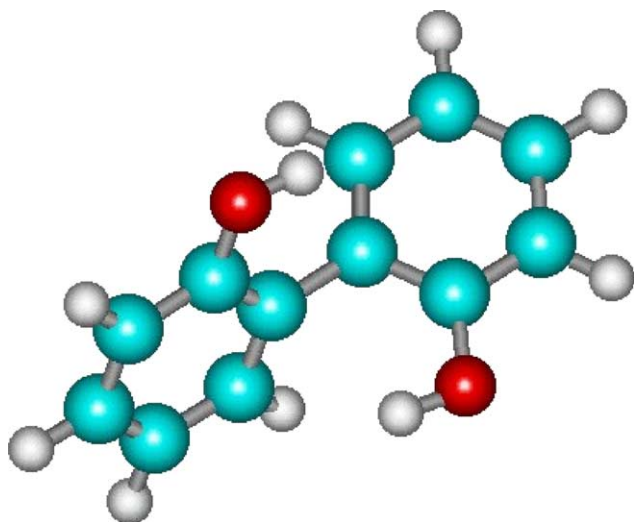


Fig. 2. Stereo drawing of 2BP: the OH groups point towards the  $\pi$  systems of the adjacent ring, suggesting the formation of O–H... $\pi$  internal hydrogen bonds.

### 3.3. Conformation, structure and theoretical calculations of 2BP

Without the data on the deuterated species, we needed the support of some theoretical calculations to corroborate the data on the normal species. The minimum energy conformation was found by performing a B3LYP/6-311++G\*\* calculations [12]. The obtained geometry, given in Table 3, gives the rotational constants  $A = 1442.2$ ,  $B = 482.8$ , and  $C = 434.4$  MHz, respectively. They are in a relatively good agreement with the experimental values (max. dev. for  $B$ , 1.8%). The calculations also suggested the only component of the dipole moment to be  $\mu_c$  (1.08 D).

We adjusted the valence angle  $\alpha$  and the dihedral angle  $\tau$  of Fig. 1, in order to reproduce more or less exactly the experimental rotational constants, obtaining  $\alpha = 119.7$  and  $\tau = 112.7$ , respectively.

### 3.4. Internal hydrogen bond

The geometry of Table 3 indicates the two OH groups to be co-planar with the respective phenyl ring, but to point

towards the adjacent ring. The H...O non-bonded distances are 3.96 Å, much longer than the AM1 value mentioned in Ref. [1]. It indicates that an internal O–H...O hydrogen bond must be ruled out. We believe the red shift of the O–H vibration is due to the O–H... $\pi$  internal hydrogen bonds, a kind of intramolecular interaction often characterized by rotational spectroscopy (Fig. 2) [13].

## 4. Conclusions

The rotational spectrum of 2BP, a member of a family of compounds characterized by enantiomeric effects, has been investigated for the first time. This has been possible employing free jet technique and heated sampling sources.

No tunneling effects due to the interconversion of two equivalent enantiomeric forms have been observed.

We could not measure the rotational spectrum of the O di-deuterated species, because of deuterium redistribution, upon heating, with the hydrogens of the aromatic rings. We are planning to observe them in the future, when vaporizing cold 2BP-O- $d_2$  species by laser ablation, a technique which is becoming to be combined with molecular beam Fourier-transform MW (MBFTMW) spectroscopy. In addition, the spectroscopic resolving power of MBFTMW is higher than that of the spectrometer used in this work, so that the enantiomeric conversion splitting could be observed with this technique.

## Acknowledgements

We are grateful to Mr A. Millemaggi for technical help. The University of Bologna, the Ministero dell'Università e della Ricerca Scientifica e Tecnologica, and the Consiglio Nazionale delle Ricerche are acknowledged for financial support.

## References

- [1] M. Lucarini, G.F. Pedulli, L. Valgimigli, R. Amorati, F. Minisci, *J. Org. Chem.* 66 (2001) 5456.
- [2] See for example: H.-D. Becker, V. Langer, J. Sieler, H.-C. Becker, *J. Org. Chem.* 57 (1992) 1883.
- [3] E. Hirota, Y. Kawashima, *J. Mol. Spectrosc.* 207 (1995) 243.
- [4] (a) See for example: W. Caminati, P. Moreschini, I. Rossi, P.G. Favero, *J. Am. Chem. Soc.* 120 (1998) 11144.  
(b) S. Melandri, A. Maris, P.G. Favero, W. Caminati, *Chem. Phys.* 283 (2002) 185.
- [5] S. Melandri, W. Caminati, L.B. Favero, A. Millemaggi, P.G. Favero, *J. Mol. Struct.* 352/353 (1995) 253.
- [6] J.K.G. Watson, in: J.R. Durig (Ed.), *Vibrational Spectra and Structure*, vol. 6, Elsevier, New York, 1977, pp. 1–89.
- [7] S. Melandri, G. Maccaferri, W. Caminati, P.G. Favero, *Chem. Phys. Lett.* 256 (1996) 513.
- [8] Y. Nosenko, A. Mordzinski, XX International Symposium on Molecular Beams, June 8–13, 2003, Lisbon, Portugal, Communication P27B.

- [9] Y. Nosenko, Y. Stepanenko, F. Wu, R.P. Thummel, A. Mordzinski, Chem. Phys. Lett. 315 (1999) 87.
- [10] T. Junk, W.J. Catallo, Chem. Soc. Rev. 26 (1997) 401.
- [11] Y. Huang, M. Sulkes, Chem. Phys. Lett. 254 (1996) 242.
- [12] Gaussian 98, Revision A.7, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S.Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M. W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, and J.A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.
- [13] See, for example, the case of *syn* allyl alcohol, S. Melandri, P.G. Favero, W. Caminati, Chem. Phys. Lett. 223 (1994) 541.