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A study of the bis(4-chlorophenyl) sulphide by ^{35}Cl nuclear quadrupole resonance and *ab initio* calculations

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Abstract. As an extension of previous works in sulphur-substituted biphenyls, a complete pulsed ^{35}Cl nuclear quadrupole resonance (NQR) study of the bis(4-chlorophenyl) sulphide compound is presented. In order to characterize the structural thermal behaviour of the solid phase, the NQR spectra and spin–lattice relaxation times were recorded from 80 K to 330 K. In addition, *ab initio* calculations at HF/3-21G* and 6-31G* levels were performed in order to obtain information about the equilibrium geometry and the torsional potential of the free bis(4-chlorophenyl) sulphide molecule. The NQR study results show that the title compound presents a unique stable crystalline phase in the scanned temperature range. This phase diagram contrasts notably with those observed at the same temperatures in bis(4-chlorophenyl) sulphone and bis(4-chlorophenyl) sulphoxide, which show an incommensurate phase transition and two-phase coexistence, respectively. The narrow NQR line observed suggests that the ^{35}Cl atoms in the unit cell are in crystallographic equivalent positions. *Ab initio* calculations for the free molecule show that the symmetry point group is C_2 and the dihedral angle is 60° . The results are discussed and compared with the known information about the sulphone and sulphoxide derivatives. The effect of the interphenyl linking group is also discussed, in order to understand the evolution of the phase diagram in this group of compounds.

1. Introduction

The study and characterization of incommensurate (IC) phases in organic molecular crystals has progressively grown in the last decade. Microscopic models for molecular crystals describing the instability of the high temperature phase, and the subsequent IC transition, deal with specific features of these kinds of solid, for example, conformational modulations [1], competition between inter- and intramolecular interactions [2] and coupling between internal and lattice degrees of freedom [3, 4]. Nevertheless, the number of Van der Waals solids exhibiting IC phases is considerably lower than the case of ionic solids [5]. This is a severe drawback in the proposal and validation of more general microscopic and phenomenological models applicable to Van der Waals solids. The success of the theoretical comprehension of the structural instabilities in ionic solids, especially in the A_2BX_4 and $AA'BX_4$ families, lies in the extensive experimental study of the phase diagrams of a great number of related

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materials [2,5]. Hence, it is convenient that the characterization of new IC molecular solids be also completed with the study of the phase diagram of several closely related derivatives. The knowledge of how the IC transition can be triggered or inhibited by these selective substitutions can be useful in order to improve the understanding of the lattice instability.

There are two structurally related organic crystals exhibiting IC phases; the biphenyl [3,4] and the bis(4-chlorophenyl) sulphone ((ClC₆H₄)₂SO₂, abbreviated to BCIPS) [6,7]. Structural transitions to IC phases occur in both compounds, showing spatial modulations of the molecular conformation. It is interesting to note that electron diffraction studies revealed a twisted conformation for the free biphenyl molecule with a dihedral angle of 42° [8]. In solid biphenyl, a planar molecular conformation is observed at room temperature, resulting from the delicate balance between intra- and intermolecular interactions [2–4]. This balance is altered at lower temperatures, causing the instability of the spatially periodic structure [3,4]. A spatial IC modulation of the dihedral angle between phenyl groups is observed at temperatures lower than 40 K [3,4]. Although similar conformational distortions are observed in the IC phase of BCIPS [6,7], including some degree of twisting with respect to the free molecule conformation, the role of the internal potentials in the lattice instability is still a matter of discussion. The results of several lattice dynamic calculations suggest that the effects of the internal potentials are secondary [9,10].

There are two close derivatives of BCIPS which can be studied in order to probe the effect of atomic substitutions. They are the bis(4-chlorophenyl) sulphoxide ((ClC₆H₄)₂SO, abbreviated to BCIPSX) and the bis(4-chlorophenyl) sulphide ((ClC₆H₄)₂S, abbreviated to BCIPSD). In this series of compounds, the oxidation degree of the sulphur atom linking the two phenyl groups is progressively reduced. BCIPSX was recently studied by ³⁵Cl nuclear quadrupole resonance (NQR), and the results showed that the IC transition is absent [11]. In this case, the solid seems to appear in an inhomogeneous or partially disordered structure. On the other hand, no structural data are available for the phase diagram of BCIPSD. This compound is especially interesting to study because a molecular conformation with C₂ symmetry like that of BCIPS is expected.

The aim of this paper is to present a preliminary structural characterization of BCIPSD, in the free and solid states. The phase diagram of BCIPSD in the temperature range 80–330 K was studied by using the ³⁵Cl NQR technique. In addition, the equilibrium conformation for the free BCIPSD molecule was calculated from *ab initio* methods, in order to evaluate conformational changes with respect to BCIPS. The results are discussed and compared with the known information about the sulphone and sulphoxide derivatives.

2. Experiment

2.1. Synthesis of bis(4-chlorophenyl) sulphide

Bis(4-chlorophenyl) sulphide was synthesized by an improved method based on an earlier procedure reported in the literature [12]. To a solution of bis(4-chlorophenyl) sulphoxide (1 g, 3.69 mmol) in methylene chloride (40 ml), 7.5 ml of acetyl chloride was added at room temperature and the reaction mixture was allowed to reach 40 °C. The progress of the reaction was monitored by thin layer chromatography using benzene:ethyl acetate (80:20) as the solvent system. After stirring the reaction mixture for 90 min at 40 °C, 10 ml of cooled water (0–5 °C) was added. The resulting white precipitate was filtered *in vacuo*, washed with cold water and dried. The obtained precipitate was purified by sublimation at 80 °C and 200 mm Hg, yielding 0.894 g of pure bis(4-chlorophenyl) sulphide

(yield 95%), m.p. 97–98 °C. $^1\text{H-NMR}$ and mass spectra were recorded on a 200.13 MHz Bruker spectrometer and a Finnigan model 3300 F-100 quadrupole mass spectrometer respectively. For aromatic protons, the $^1\text{H-NMR}$ (DMSO-d_6) spectrum reveals a characteristic AA'BB' system with two doublets, one centred at $\delta_H = 7.56$ ppm for H-3, 5 and the other centred at $\delta_H = 7.46$ ppm for H-2, 6 according to similar assignments for this compound in chloroform [13]. For each mass/charge (m/z) observed ratio, the following isotopic abundance percentages were yielded by mass spectroscopy: m/z (%), 257 (10.5), M^+ , $^{37}\text{Cl}^{37}\text{Cl}$; 255 (59.2), M^+ , $^{35}\text{Cl}^{37}\text{Cl}$; 253 (81.8), M^+ , $^{35}\text{Cl}^{35}\text{Cl}$. These values correspond to the molecular structure of BCIPSD.

2.2. NQR measurements

The synthesized sample of BCIPSD was packed *in vacuo* into a glass cylinder of 1 cm diameter and 2.5 cm length. Measurements of the ^{35}Cl NQR lineshape and spin–lattice relaxation time (T_1) were performed from 80 K to 330 K. The NQR lineshape was obtained from the fast Fourier transform (FFT) of the half-echo signal following the $\pi/2-\tau_E-\pi$ Hahn pulse sequence [14].

The T_1 measurements were performed by the standard three pulse sequence ($\pi/2-\tau-\pi/2-\tau_E-\pi$), with an echo time τ_E of 200 μS . Measurements of the spin–spin relaxation time (T_2) were also performed at 80 K, 117 K, 300 K and 337 K. The T_2 measurements were performed using the Hahn pulse sequence $\pi/2-\tau-\pi$. The $\pi/2$ pulses were 23 μS in width. The $S(\tau)$ amplitudes of the FFT of the echo signal following the π pulse in the Hahn sequence are related to τ by the expression:

$$S(\tau) = S_0 \exp(-2\tau/T_2).$$

The T_2 values were obtained by fitting the above expression. The NQR spectrometer used to measure the ^{35}Cl NQR signals in the BCIPSD has been described elsewhere [15]. The spectrometer temperature control provides temperature stability of the sample better than 0.1 K during the measurements.

3. Experimental results

The temperature behaviour of the NQR frequency is plotted in figure 1. Qualitatively, the observed temperature dependence agrees with the expected behaviour in molecular crystals [16]. The inset in figure 1 shows a typical ^{35}Cl NQR spectra of the sample at 83.7 K. The NQR line shape is Lorentzian, with a half width of about 1 kHz in the whole temperature range.

Following the Bayer–Kushida model for the molecular torsional oscillations, the temperature dependence of ν_Q between 80 K and 330 K can be fitted by [16]:

$$\nu_Q(T) = \nu_0 - \sum_j \frac{3}{4} \left(\frac{\hbar\nu_0}{I_j\omega_j} \right) \coth \left(\frac{\hbar\omega_j}{2k_B T} \right). \quad (1)$$

In this expression, ω_j is the j th torsional frequency of the j th mode, I_j is a quantity with units of moment of inertia associated with that mode and ν_0 is the NQR frequency in a fictitious 'static' lattice.

In order to obtain the best fit of the experimental data it was necessary to assume only one dominant mode ($j = 1$) in the Bayer–Kushida expression (1), and to introduce a temperature dependence of ω in the form: $\omega = \omega_0(1 - g_1T + g_2T^2)$. The parameters obtained from the least-squares fit of (1) to experimental data are shown in table 1. The orders of magnitude of ω_0 and I are expected in crystalline ordered phases of chlorine-substituted biphenyl-type compounds

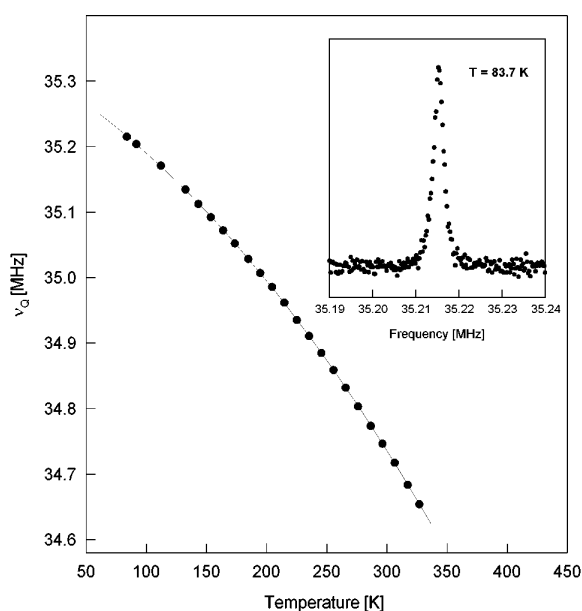


Figure 1. Temperature behaviour of the ^{35}Cl NQR (ν_Q) frequencies in BCIPSD. The inset shows the ^{35}Cl NQR spectrum of BCIPSD at 83.7 K.

Table 1. Parameters obtained from a Bayer–Kushida fit of the thermal behaviour of the NQR frequency (ν_Q) for the family of $(\text{ClC}_6\text{H}_4)_2\text{X}$ ($\text{X} = \text{SO}_2, \text{SO}, \text{S}$) compounds.

Compound	ν_0 (MHz)	I ($\text{amu } \text{Å}^2$)	ω_0 (cm^{-1})	g_1 ($\text{K}^{-1} \times 10^{-4}$)	g_2 (K^{-2})
BCIPSD	35.33	2900	120	10	7×10^{-7}
BCIPSX	35.00/35.06	2800/3000	130/130	4.5/5.5	—
BCIPS	35.16	3200	80	2.7	—

with ω_0 frequencies less than 200 cm^{-1} and with moments of inertia of about $10^3 \text{ amu } \text{Å}^2$. Alternatively, a least-squares fit was checked out, including two oscillation modes ($n = 2$) in the Bayer–Kushida expression (1). In this case a linear temperature behaviour for ω was adopted; however, the results obtained from this fit were unsatisfactory. From table 1 it can be seen that the rigid lattice frequencies, ν_0 , of the three related compounds are indistinguishable within 1%. It can also be observed that the ω_0 frequencies of the BCIPSD and BCIPSX are very close to each other and they are slightly greater than the ω_0 of BCIPS.

The ^{35}Cl spin–lattice relaxation time experimental data are shown in figure 2. The log–log plot is linear in the whole temperature range. This kind of behaviour is associated with the molecular torsional oscillation model [16] where: $T_1 = AT^{-\lambda}$. The resulting fitting parameters for T_1 using this expression are: $A = (1.7 \pm 0.3) \times 10^7 \text{ ms K}^{-\lambda}$; $\lambda = 2.25 \pm 0.04$. The values of these parameters are in agreement with those expected for ordered molecular crystals [16], where λ takes values slightly above 2.

The experimental data for ^{35}Cl spin–spin relaxation time T_2 are shown in table 2. No significant variations were noted within the observed temperature range. The T_2 values obtained are similar to those observed in BCIPS [17].

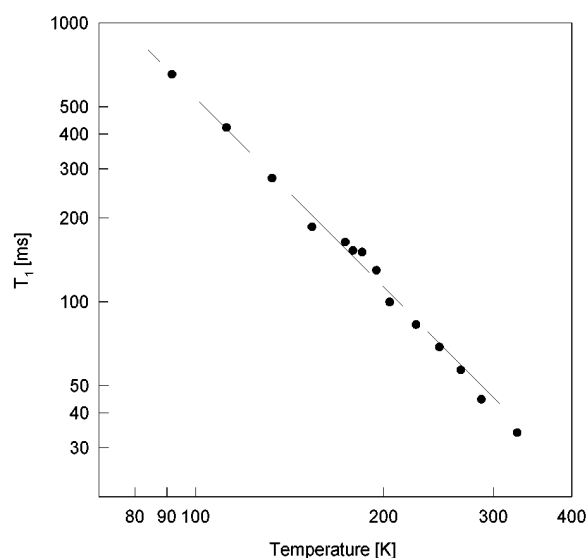


Figure 2. Log-log plot of the temperature behaviour of the spin-lattice relaxation time T_1 of BCIPSD. Points: experimental data. Solid line: fitting of the torsional oscillation expression $T_1 = AT^{-\lambda}$.

Table 2. Some experimental values of the T_2 spin-spin relaxation time in BCIPSD.

Temperature (K)	T_2 (μ s)
79.7	(566 \pm 27)
117.2	(534 \pm 7)
299.4	(657 \pm 28)
337.1	(656 \pm 25)

4. *Ab initio* calculations

Using the quantum chemistry package SPARTAN [18], *ab initio* calculations at the HF/6-31G* level were performed in order to determine the equilibrium free-molecule conformation of BCIPSD. A C_2 symmetry resulted for the free molecule. A schematic view of the BCIPSD molecule is shown in figure 3. Some geometrical parameters of the equilibrium conformation are summarized in table 3. The bond lengths obtained for BCIPSD are consistent with average values reported for C_{ar} -S and C_{ar} -Cl aromatic bond types [19, 20]. For the sake of comparison some of these values were included in table 3. The calculated C_1 -S- $C_{1'}$ angle $\alpha = 102.5^\circ$ (see figure 3) is near the tetrahedral angle and differs by about 5% from the reported value $\alpha' = 107^\circ$ of the diphenyl sulphide [21]. On the other hand, the obtained value for the dihedral angle $\varphi = 60^\circ$ between the phenyl ring and the C_1 -S- $C_{1'}$ plane (see figure 3), is significantly different from the result of $\varphi = 90^\circ$ in BCIPS calculated using the same method [10].

In addition, the shape of the torsional potential for the BCIPSD molecule as a function of the dihedral angle φ was obtained by means of *ab initio* calculations at the HF/3-21G* level. This method was chosen in order to obtain a relatively fast estimation of the potential profile. Figure 4 shows the resulting plot for the BCIPSD molecule, taking the energy at the

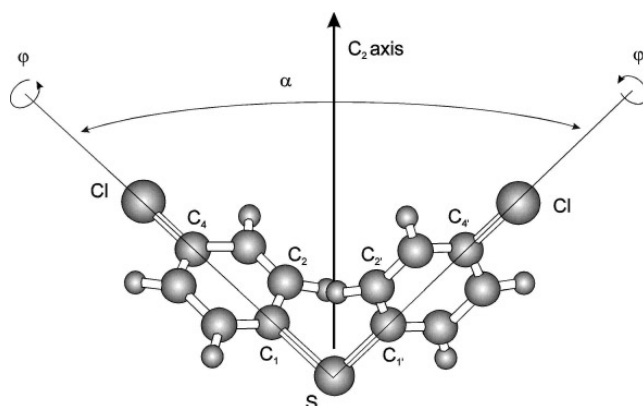


Figure 3. Schematic view of the free molecule of BCIPSD. The C_2 axis lies on the Cl–S–Cl plane. The φ label indicates the dihedral angle between each benzene ring and the C_1 –S– $C_{1'}$ plane.

Table 3. Symmetry point group, bond lengths and angles of BCIPSD, obtained from *ab initio* 6-31G* calculations. Comparison with values found in the literature for C_{ar} –S and C_{ar} –Cl bonds in aromatic compounds and the $\angle C_1$ –S– $C_{1'}$ angle in diphenyl sulphide and 4-amino-4-nitrodiphenyl sulphide (abbreviated to RSD).

	Point group	φ ($^\circ$) (dihedral)	Bend ($^\circ$) ($\angle C_1$ –S– $C_{1'}$)	C_{ar} –S bond (\AA)	C_{ar} –Cl bond (\AA)
BCIPSD ^a	C_2	60	102.5	1.787	1.742
Aromatic compounds			107 ^b	1.768 ± 0.01^c	1.739 ± 0.01^c
RSD			103.9 ± 0.3^d		

^a This work.

^b [21].

^c [19].

^d [20].

equilibrium conformation as the reference. Each point of the curve was obtained imposing C_2 symmetry, fixing the φ angle and relaxing all the structural parameters of the molecule. As can be seen in figure 4, the energy profile is rather flat for φ angles between 40 and 90°. In this range, the variation of the molecular energy is below 0.5 kcal mol⁻¹. To check the value ΔE of the energy barrier at $\varphi = 90^\circ$, calculations with the more accurate 6-31G* basis were also performed. The obtained value was $\Delta E = 0.43$ kcal mol⁻¹, which in fact is comparable with that obtained with the 3-21G* basis. As can be seen, the energy required to twist the phenyl groups in the free molecules of BCIPSD is very low. These energy values are comparable with the magnitude of the intermolecular interactions in the solid phase. Great differences in the twist angle of BCIPSD molecule can therefore be expected between the solid and gas phases.

Using the HF/6-31G* method, the electric dipole moment for BCIPSD was estimated as $\mu_{SD} = 0.43$ D. This value agrees with $\mu = 0.44$ D obtained by the method of vector addition of bond moments [21, 22] and differs by about 25% from the experimental value $\mu_{ex} = 0.58$ D [22]. In BCIPS and BCIPSD, the molecular dipole vectors are orientated along the symmetry axis, but pointing in opposite directions as expected from the relative electronegativity value of the SO₂ group.

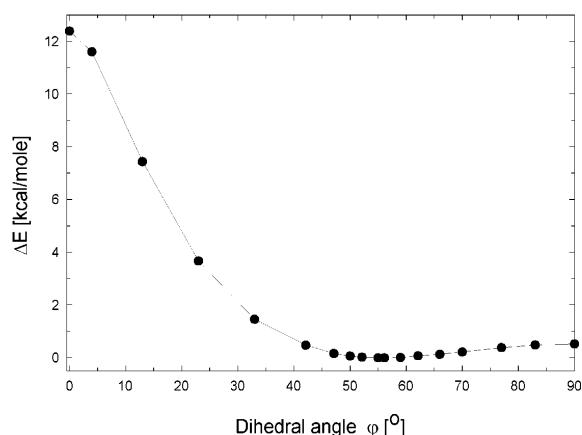


Figure 4. Molecular energy as a function of the dihedral angle ϕ between the benzene ring and the $C_1-S-C_{1'}$ plane for BCIPSD. The C_2 conformation at $\phi = 60^\circ$ was chosen as a reference for the energy values.

5. Concluding remarks

This first NQR study of BCIPSD shows that its phase diagram is quite different from those observed for BCIPS and BCIPSX in the same temperature range. In its solid state, BCIPSD presents an ordered crystalline structure which is stable in the temperature range 80–330 K. The unique and narrow line observed in the NQR spectra shows that the ^{35}Cl atoms in the unit cell are placed in equivalent crystallographic positions. In fact, the equivalence of the two chlorine atoms in the molecule demonstrates that BCIPSD molecules are located in sites possessing C_2 or higher symmetry.

On the other hand, *ab initio* calculations indicate that the free molecules of BCIPSD and BCIPS present some geometrical differences. The dihedral angle value $\phi = 60^\circ$ obtained for BCIPSD is far from the $\phi = 90^\circ$ value for BCIPS. Phenyl rings of BCIPSD are therefore notably twisted with respect to BCIPS. The symmetry point group resulting in the free molecules of BCIPSD is C_2 . The mirror symmetry plane present in the free molecules of BCIPS is lost in BCIPSD.

For BCIPSD and BCIPS, the resulting shape of the isolated molecule static energy as a function of the dihedral angle ϕ is rather flat. The energy ΔE required to twist the phenyl rings seems to be very low, irrespective of the X group linking them. In the case of BCIPSD, appreciable twisting can be produced with energies lower than $\Delta E = 0.43 \text{ kcal mol}^{-1}$. The molecular conformation in the solid will then depend on the magnitude of intermolecular interactions.

For molecular crystals whose molecules have moments μ lower than 1 D, the value of the dipole contribution to the lattice energy must be almost negligible since this contribution is proportional to the square of the dipole moment. However, the dipole interactions can affect the properties of a molecular crystal, in particular, the establishment of its equilibrium structure [23]. Because of this, in the solid phase of the family of $(\text{ClC}_6\text{H}_4)_2\text{X}$ ($\text{X} = \text{SO}_2, \text{SO}, \text{S}$) compounds, these interactions can be an important factor in determining the molecular conformation. Therefore, although the X group contributes to the determination of the equilibrium molecular conformation of the free molecules, in the solid phase this conformation can be easily altered (see figure 4). Indeed, the experimental evidence shows that similar

substituted diphenyl sulphides do not exhibit a preferred orientation of their phenyl rings in the solid phase, as would occur from purely intramolecular effects [20, 24]. In this way, the dihedral angle φ for the BCIPSD molecule in the solid should assume a value inside the interval 40 to 90°.

Acknowledgments

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