Three atropisomers of biphenyl: twist by tunable *para* substituents

RAMESH KARUPNASWAMY and PRABUSANKAR GANESAN*

Department of Chemistry, Indian Institute of Technology Hyderabad, Kandi, Sangareddy, Telangana 502 285, India

E-mail: prabu@iith.ac.in

MS received 8 February 2018; revised 20 March 2018; accepted 20 March 2018; published online 30 June 2018

Abstract. The geometrical twist of aryl-aryl bond in biphenyl by weakly coordinating anion and selone at the *para* position has not been clear so far. We report here the synthesis and investigation into the diverse structural properties of biphenyl with weakly coordinating biphenyl imidazolium salts and neutral imidazole selone that exhibit three atropisomers of biphenyl. The approaches underline the diversity of the effects of *para* substituent with dynamic nature at biphenyl molecule.

Keywords. Biphenyl rotation; fluxional molecule; imidazole; selone.

1. Introduction

The tunable dihedral or twist angle (ϕ) of biphenyl derivatives have garnered long-standing attention due to their potential application in molecular electronics¹⁻³ and catalytic transformations.⁴ As shown in Scheme 1, the biphenyl is known to exist from 45° to 90° twist angle in the gaseous state due to *ortho* substituent repulsion,^{5,6} while the biphenyl appears to be planar in the crystalline state at room temperature due to π -electron delocalization.^{7,8} It is clear that the controlled tunability of biphenyl ring by suitable substituent is paramount,⁹ as these characteristics are key to adapting the unique structural and electronic demands of materials. However, the ostensible structural inconsistency was observed with substituted biphenyl. Indeed the exhaustive survey was carried out by Grein *et al.*, in 2002 to understand the relationship between twist angles and rotation energy barriers of biphenyl and substituted biphenyls using high-level Hartree-Fock and density functional calculations.¹⁰ Therefore, the steric factor plays a major role in the structures of mono substituted and *meta* disubstituted biphenyls. Whereas in the case of *ortho* dichloro biphenyl, the attractive force between two halogen atoms was considered.

Later, the rotation at biphenyl with a single *ortho*-substituent was demonstrated by Mazzanti *et al.*¹¹ Recently Masson *et al.*, demonstrated the consequences of subtle changes to the biphenyl rotation.¹² However, compared to *ortho* and *meta* substituted biphenyl derivatives,¹³ the net effect of *para* substituent on biphenyl ring is limited.¹⁴ As of our knowledge, the aryl-aryl twist in biphenyl mediated by tunable *para* substituent has not been documented. In order to gain further insight into the structural features of tunable *para*-substituted biphenyl species, we have examined the synthesis of 4,4'-substituted biphenyl and explored their structural diversity through anion exchange and selenation.

2. Experimental

2.1 General consideration

All manipulations were carried out under an argon atmosphere using Schlenk line techniques. The solvents were purchased from commercial sources and purified according to standard procedures.¹⁵ 4,4'-bis(chloromethyl)-1,1'-biphenyl, selenium powder, acetonitrile, toluene, methanol, and potassium carbonate were purchased from commercial sources. FT-IR measurements were carried out on a Bruker Alpha-P Fourier Transform spectrometer. NMR spectra were recorded on Bruker Ultra shield 400 spectrometers at 25 °C, unless otherwise stated. Chemical shifts are given relative to TMS and

*For correspondence

Scheme 1. Structure of biphenyl. Crystalline state: $\phi = 0^\circ$. Gaseous state: $\phi = 45^\circ\text{--}90^\circ$.

were referenced to the solvent resonances as internal standards. Single crystals of **2** and **3** for the single crystal analysis were obtained from their saturated solutions in methanol, layered with hexane at room temperature, while **4** was obtained from its saturated solutions in chloroform, layered with hexane at room temperature. Suitable single crystals for X-ray structural analysis of **2–4** were mounted at room temperature in inert oil under liquid nitrogen condition. Using Olex2,¹⁶ the structure was solved with the ShelXS^{17,18} structure solution program using Direct Methods and refined with the olex2.refine refinement package using Gauss-Newton minimization. Absorption corrections were performed on the basis of multi-scans. Non-hydrogen atoms were anisotropically refined. No restraint has been made for any of the compounds. **2** depicted both “A level and B level alerts” due to a very high thermal parameter of isopropyl groups as well as disordered BF_4^- ions. Attempts to resolve the alerts for **2** by alternative space group, $P2_1/c$ were not successful. **3** gave both “A level and B level alerts” due to a very high thermal parameter of isopropyl groups. A minor “B level alert in **4** that is associated with ‘MainMol’ Ueq as compared to neighbors of C11 is due to the thermal parameter differences between C11 and neighboring atom.

2.2 Synthesis of 1

Freshly prepared 1-isopropyl imidazole (2.3 mL, 49.8 mmol) was added to 4,4'-bis (chloromethyl)-1,1'-biphenyl (2.0 g, 19.9 mmol) in acetonitrile (20 mL) under argon atmosphere. The reaction mixture was refluxed for 48 h at 85°C . The reaction progress was monitored by TLC. After completion of the reaction, the product **1** was formed as a white precipitate. Yield: 97% (based on 4,4'-bis(chloromethyl)-1,1'-biphenyl). M.p.: $108\text{--}110^\circ\text{C}$. Elemental analysis calcd. (%) for $\text{C}_{26}\text{H}_{32}\text{N}_4\text{Cl}_2$ (471.47): C, 66.24; H, 6.84; N, 11.88; Found: C, 66.1; H, 6.7; N, 11.7. ^1H NMR (D_2O , 400MHz): $\delta = 7.56\text{--}7.54$ (d, 4H, ImH), $7.38\text{--}7.34$ (m, 8H, ArH), 5.29 (s, 4H, NCH_2), $4.54\text{--}4.44$ (sept, 1H, $^i\text{PrCH}$), $1.40\text{--}1.39$ (d, 12H, $^i\text{PrCH}_3$). ^{13}C NMR (D_2O , 100 MHz): $\delta = 143.08$ (ImCH), 136.13 ($\text{ArCH}_{\text{ipso}}$), 131.96 ($\text{ArCH}_{\text{ortho}}$), 130.42 ($\text{ArCH}_{\text{meta}}$), 125 (ImCH), 123.61 (ImCH), 55.99 ($^i\text{PrCH}$), 55.17 (NCH_2), 24.67 ($^i\text{PrCH}_3$). FT-IR (neat): $\bar{\nu} = 3426$ (w), 3366 (w), 3120 (w), 3047 (s), 2971 (w), 1617 (w), 1557 (s), 1543 (m), 1502 (m), 1461 (m), 1415 (m), 1331 (m), 1267 (m), 1176 (s), 1140 (s), 854 (s), 789 (s), 748 (s), 654 (s), 611 (s) cm^{-1} .

2.3 Synthesis of 2

To a stirred solution of **1** (0.2 g, 0.4 mmol) in methanol (3 mL), ammonium tetrafluoroborate (1.7 g, 1.1 mmol) was added, and the reaction mixture was stirred for 4 h at room temperature. After completion of the reaction, the mixture was evaporated under reduced pressure to get crude solid which was further washed with water (25 mL), and the solid was dissolved in methanol (8 mL) and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure to get analytically pure white solid **2**. Yield: 75% (based on **1**). M.p.: $128\text{--}130^\circ\text{C}$. Elemental analysis calcd. (%) for $\text{C}_{26}\text{H}_{32}\text{B}_2\text{N}_4\text{F}_8$ (574.17): C, 54.39; H, 5.62; N, 9.76; Found (%): C, 54.4; H, 5.5; N, 9.7. ^1H NMR ($\text{DMSO-}d_6$, 400MHz): $\delta = 9.41$ (s, 2H, ImH), $7.94\text{--}7.86$ (d, 4H, ImH), $7.76\text{--}7.74$ (d, 4H, $\text{ArH}_{\text{ortho}}$), $7.56\text{--}7.54$ (d, 4H, ArH_{meta}), 5.46 (s, 4H, NCH_2), $4.71\text{--}4.61$ (sept, 1H, $^i\text{PrCH}$), $1.51\text{--}1.49$ (d, 12H, $^i\text{PrCH}_3$). ^{13}C NMR ($\text{DMSO-}d_6$, 100 MHz): $\delta = 139.72$ (ImCH), 134.97 (ArC_{ipso}), 129 ($\text{ArCH}_{\text{ortho}}$), 134.22 ($\text{ArCH}_{\text{meta}}$), 121 (ArC_{para}), 122.60 (ImCH), 127.28 (ImCH), 52.40 ($^i\text{PrCH}$), 51.61 (NCH_2), 22.22 ($^i\text{PrCH}_3$). ^{11}B NMR ($\text{DMSO-}d_6$, 128.4 MHz): $\delta = 1.25$ (s, BF_4^-). ^{19}F NMR ($\text{DMSO-}d_6$, 376.4 MHz): $\delta = 148.18$ (s, BF_4^-). FT-IR (neat): $\bar{\nu} = 3155$ (m), 1624 (w), 1558 (m), 1449 (m), 1157 (w), 1031 (s), 863 (w), 831 (m), 762 (w), 746 (m), 699 (m), 655 (m), 611 (w) cm^{-1} .

2.4 Synthesis of 3

To **1** (0.2 g, 0.4 mmol) in water (3 mL), KPF_6 (0.2 g, 1.3 mmol) in water (3 mL) was added under stirring condition. A white precipitate was formed immediately and refluxed for 5 h to afford white precipitate in good yield. The precipitate was filtered and washed with methanol. This was further dissolved in acetone, dried over sodium sulfate, filtered and the solvent was evaporated under reduced pressure to afford an analytical pure compound **3**. Yield: 86% (based on **1**). M.p.: $140\text{--}142^\circ\text{C}$. Elemental analysis calcd. (%) for $\text{C}_{26}\text{H}_{32}\text{N}_4\text{F}_{12}\text{P}_2$ (690.49): C, 45.23; H, 4.67; N, 8.11; Found (%): C, 45.2; H, 4.6; N, 8.1. ^1H NMR ($\text{DMSO-}d_6$, 400MHz): $\delta = 9.41$ (s, 2H, ImH), $7.93\text{--}7.86$ (d, 4H, ImH), $7.77\text{--}7.75$ (d, 4H, $\text{ArH}_{\text{ortho}}$), $7.56\text{--}7.54$ (d, 4H, ArH_{meta}), 5.46 (s, 4H, NCH_2), $4.71\text{--}4.62$ (m, 1H, $^i\text{PrCH}$), $1.52\text{--}1.50$ (d, 12H, $^i\text{PrCH}_3$). ^{13}C NMR ($\text{DMSO-}d_6$, 100 MHz): $\delta = 139.74$ (ImCH), 134.97 (ArC_{ipso}), 128.98 ($\text{ArCH}_{\text{ortho}}$), 127.29 ($\text{ArCH}_{\text{meta}}$), 134.19 (ArC_{para}), 120.99 (ImCH), 122.60 (ImCH), 52.41 ($^i\text{PrCH}$), 51.64 (NCH_2), 22.19 ($^i\text{PrCH}_3$). ^{31}P NMR ($\text{DMSO-}d_6$, 161 MHz): $\delta = 157.33\text{--}130.98$ (septet, PF_6^-). ^{19}F NMR ($\text{DMSO-}d_6$, 161 MHz): $\delta = 71.03\text{--}69.14$ (d, PF_6^-). FT-IR (neat): $\bar{\nu} = 3156$ (w), 1555 (m), 1175 (w), 1145 (m), 829 (s), 751 (m), 655 (m), 556 (m) cm^{-1} .

2.5 Synthesis of 4

1 or **2** or **3** (4.3 mmol), activated potassium carbonate (1.8 g, 12.8 mmol), Se powder (0.4 g, 5 mmol), and methanol (25 mL) were added under argon atmosphere. The reaction

Scheme 2. Synthesis of 1–4.

mixture was refluxed for 36 h at 70 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, water was added to the reaction mixture and extracted with dichloromethane (3×15 mL). The organic extract was washed with Na_2SO_4 and evaporated under reduced pressure. Yield: 56–62% (based on **1** or **2** or **3**). M.p.: 198–200 °C. Elemental analysis calcd. (%) for $\text{C}_{26}\text{H}_{30}\text{N}_4\text{Se}_2$ (556.46): C, 56.12; H, 5.43; N, 10.07; Found (%): C, 56.0; H, 5.3; N, 10.0. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.54–7.52 (d, 4H, $\text{ArH}_{\text{ortho}}$), 7.41–7.39 (d, 4H, ArH_{meta}), 6.95 (d, 2H, ImH), 6.86 (d, 2H, ImH), 5.42 (s, 4H, NCH_2), 5.29–5.21 (sept, 2H, $i\text{PrCH}$), 1.41–1.40 (d, 12H, $i\text{PrCH}_3$). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 154.94 (C=Se), 119.02 (ImCH), 115.53 (ImCH), 140.27

(ArC_{ipso}), 128.84 ($\text{ArCH}_{\text{ortho}}$), 127.42 ($\text{ArCH}_{\text{meta}}$), 134.89 (ArC_{para}), 52.26 ($i\text{PrCH}$), 51.20 (NCH_2), 22 ($i\text{PrCH}_3$). FT-IR (neat): $\bar{\nu}$ = 3080(w), 2974(w), 1990(w), 1662(m), 1562(m), 1499(m), 1452(m), 1423(m), 1398(vs), 1363(m), 1287(w), 1220(s), 1186(m), 1133(w), 1043(m), 747(s), 670(m) cm^{-1} .

3. Results and Discussion

3.1 Synthesis and characterization of 1–4

The water-soluble and hygroscopic salt **1** was obtained in excellent yield by treating freshly prepared

1-isopropyl imidazole with 4,4'-bis (chloromethyl)-1, 1'-biphenyl in acetonitrile (Scheme 2). The counter ion chloride was conveniently exchanged by tetrafluoroborate or hexafluorophosphate to yield **2** and **3**, respectively (Scheme 2). **1–3** are soluble in highly polar solvents like DMSO, MeOH and water. The salts **1–3** were characterized by CHN analysis, FTIR, ^1H NMR and ^{13}C NMR techniques. In ^1H NMR, the imidazolium CH peak in **2** and **3** appeared at δ 9.41, while it is absent for **1** due to proton exchange by deuterium. In addition, the tetrafluoroborate salt (**2**) and hexafluorophosphate salt (**3**) were further confirmed by ^{19}F NMR, ^{31}P NMR and ^{11}B NMR spectroscopy. The ^{11}B NMR spectrum of **2** showed a sharp signal in the range of δ 1.25 and ^{19}F NMR spectra of **2** showed a sharp signal at δ 148.18. The ^{31}P NMR spectrum of **3** depicted a septet in the range of δ 157.33–130.98 and ^{19}F NMR spectra of **3** gave doublet at δ 71.03–69.14.

The selone **4** was isolated in good yield from the reaction between **1** or **2** or **3**, and 1.1 equivalences of Se in the presence of six equivalences potassium carbonate (Scheme 2). The formation of **4** was confirmed by FT-IR, elemental analysis and multinuclear NMR (^1H , and ^{13}C). The FT-IR spectrum of **4** depicts the C=Se bond stretching frequency at 1220 cm^{-1} . In ^1H NMR, the $-\text{CH}-\text{CH}-$ protons of the imidazole rings in **4** are (δ 6.95 and 6.86) significantly upfield shifted compared to that of corresponding imidazolium salts (δ 7.56–7.54 for **1**, δ 7.94–7.86 for **2** and δ 7.93–7.86 for **3**). In ^{13}C NMR, the N-C(Se)-N carbon in **4** is (δ 154.94) about δ 12–15 shifted downfield compared with N-CH-N carbon in **1–3** (δ 143.08 for **1**, δ 139.72 for **2** and δ 139.74 for **3**). Besides, C=Se carbon chemical shift value of **4** is upfield shifted (δ 7) from those of the corresponding ligand $\text{IPr}=\text{Se}$ (δ 162.2),¹⁹ due to a decrease in the π -acceptance nature of **4**. The DEPT spectrum of **4** depicts the existence of CH_2 , CH_3 and CH groups that are in accordance with the structure of **4**.

3.2 Solid state structure of 2–4

The solid-state structures of **2–4** were unambiguously determined by single crystal X-ray diffraction technique. **2–4** crystallized in monoclinic space group, Pc for **2**, $P2_1/c$ for **3** and **4**. The solid-state structures of **2–4** are shown in Figure 1 along with selected bond distances and bond angles. **2** and **3** are ionic salts, while **4** is a neutral molecule. The imidazolium charges in **2** are balanced by two tetrafluoroborate anions, while two hexafluorophosphate ions are balancing out the imidazolium charges in **3**. Notably, the orientation of biphenyl group and five-membered N-heterocyclic moieties in **2–4** are not comparable. The N-C bond distances of

Figure 1. Solid state structures of **2–4**. Selected bond distances [$\text{\AA}$] and angles [$^\circ$]: for **2**: C(1)–N(1), 1.250(12); C(1)–N(2), 1.310(10); N(3)–C(21), 1.305(10); N(4)–C(21), 1.312(11); N(2)–C(1)–N(2), 110.1(9) and N(4)–C(21)–N(3), 112.1(9) for **3**: C(1)–N(1), 1.342(7); C(1)–N(2), 1.312(6); N(4)–C(21), 1.328(7); N(3)–C(21), 1.329(7); N(2)–C(1)–N(1), 108.2(5) and N(4)–C(21)–N(3), 109.1(5). For **4**: C(1)–N(1), 1.363(5); C(1)–N(2), 1.354(5); C(1)–Se(1), 1.825(4); N(2)–C(1)–N(1), 105.0(4).

N-C-N are not comparable. Within **2** and **3**, the N-C bond distances are not comparable, while the N-C bond distances are equal in **4**. This can be attributed to the good π overlap between N-C(Se)-N. Besides, a gradual increase in the N-C bond distances is observed from **2**, **3** to **4**. The N-C-N bond angles in **2** are slightly wider than that of **3**. Upon selenation, a considerable decrease in the N-C-N bond angle was observed for **4** compared to **2** and **3**. The C=Se bond distance in **4** is 1.825(4) $\text{\AA}$, which is comparable with that of $\text{IPr}=\text{Se}$ (1.853 $\text{\AA}$),²⁰ 4,4'-bis(N,N'-methyl imidazole-2-selone)-1,1'-biphenyl (C=Se, 1.874 $\text{\AA}$), and 4,4'-bis(N,N'-methyl-N'-allyl imidazole-2-selone)-1,1'-biphenyl (C=Se, 1.850 $\text{\AA}$).²¹

Figure 2. The atropisomers of phenyl and geometrical orientation of N-heterocyclic rings in 2–4.

3.3 Geometrical orientation of 2–4

As shown in Figure 2, the geometrical orientation of phenyl and N-heterocyclic rings are different in 2–4. In 2 and 4, the phenyl rings are nearly on the same plane, while two N-heterocyclic rings are in *trans* position. Interestingly, the geometrical orientation of phenyl rings in 3 is considerably twisted to each other and imidazolium rings are in *trans* orientation. Interestingly, the biphenyl twist angle of 3 is nearly comparable with that of 2,2′-difluoro biphenyl (57.6°).²² Thus, the torsion angles between phenyl rings in 2–4 are not comparable (−3.61° for 2, 53.21°

for 3 and 5.12° for 4). Interestingly, the biphenyl twist angle observed in 4 is considerably wider than that of 4,4′-bis(N,N′-methyl imidazole-2-selone)-1,1′-biphenyl (−0.47°), and 4,4′-bis(N-methyl-N′-allyl imidazole-2-selone)-1,1′-biphenyl (2.99°).²¹ Similarly, the torsion angles between the phenyl and N-heterocyclic ring are distinctly different (60.90° and −52.36° for 2; 86.11° and 73.81° for 3; 43.57° and −43.57° for 4). Therefore, the molecular packing of 2–4 is quite exciting. 2 and 3 are arranged in a three-dimensional network with extensive F⋯H hydrogen bonding interaction between weakly coordinating anion and imidazolium moiety. Besides, the molecular

orientation and hydrogen bonding interactions were further confirmed on the basis of 2D (HSQC and HMBC) NMR experiments (See Supporting Information).

4. Conclusions

In summary, we have synthesized and characterized the biphenyl with ionic imidazolium salts and neutral imidazole selone at *para* position. The structural properties of biphenyl with weakly coordinating biphenyl imidazolium salts and neutral imidazole selone have been demonstrated to exhibit three atropisomers of biphenyl in the solid state, unique to that of the *para*-substituted diphenyl analogues. The minor twist at biphenyl moiety gave notable changes in the solid packing of ionic imidazolium salts and neutral imidazole selone molecule. Similarly, the increase in the bulkiness at N-substituent from methyl to allyl and isopropyl at imidazole selone depicted a notable twist at biphenyl ring. However, the results indicate that substantial work remains to be accomplished in order to translate our understanding of corresponding carbene metal and chalcogenone metal derivatives for stereoselective catalytic reactions. This is the subject of ongoing investigations in our group.

Supplementary Information (SI)

FT-IR, NMR spectra and packing diagram are available at www.ias.ac.in/chemsci. CCDC 1822980-1822982 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

We gratefully acknowledge the CSIR, New Delhi (01(2884)/17/EMR-II) for financial support. RK thanks UGC for the fellowship.

References

- Kudernac T, Ruangsapichat N, Parschau M, Maciá B, Katsonis N, Harutyunyan S R, Ernst K and Feringa B L 2011 Electrically driven directional motion of a four-wheeled molecule on a metal surface *Nature* **479** 208
- Chuhmanov E P, Ermolaev N L, Plakhutin B N and Ignatov S K 2018 Tris(perfluoroalkyl)germylethynyl derivatives of biphenyl containing ferrocenyl donor group: Structure, spectra, and photoinduced intramolecular electron transfer comput *Theor. Chem.* **1123** 50
- Maier F and Trapp O 2013 The stereodynamics of 5,5'-disubstituted BIPHEPs *Chirality* **25** 126
- Fischer F, Siegle A F, Checinski M, Fischer C, Kral K, Thede R, Trapp O and Hapke M 2016 Synthesis of naphthylpyridines from unsymmetrical naphthylheptadiynes and the configurational stability of the biaryl axis *J. Org. Chem.* **81** 3087
- Bastiansen O and Samdal S 1985 Structure and barrier of internal rotation of biphenyl derivatives in the gaseous state: Part 4. Barrier of internal rotation in biphenyl, perdeuterated biphenyl and seven non-*ortho*-substituted halogen derivatives *J. Mol. Struct.* **128** 115
- Almenningen A, Bastiansen O, Fernholt L, Cyvin B N, Cyvin S J and Samdal S 1985 Structure and barrier of internal rotation of biphenyl derivatives in the gaseous state: Part 1. The molecular structure and normal coordinate analysis of normal biphenyl and perdeuterated biphenyl *J. Mol. Struct.* **128** 59
- Charbonneau G P and Delugeard Y 1976 Structural transition in polyphenyls. III. Crystal structure of biphenyl at 110 K *Acta Crystallogr.* **B32** 1420
- Cailleau H, Girard A, Moussa F and Zeyen C M E 1979 Inelastic neutron scattering study of structural phase transitions in polyphenyls *Solid State Commun.* **29** 259
- Barton D H R 1970 The principles of conformational analysis *Science* **169** 539
- Grein F 2002 Twist angles and rotational energy barriers of biphenyl and substituted biphenyls *J. Phys. Chem. A* **106** 3823
- Mazzanti A, Lunazzi L, Minzoni M and Anderson J E 2006 Rotation in biphenyls with a single *ortho*-substituent *J. Org. Chem.* **71** 5474
- Masson E 2013 Torsional barriers of substituted biphenyls calculated using density functional theory: a benchmarking study *Org. Biomol. Chem.* **11** 2859
- Lorentzen M, Kalvet I, Sauriol F, Rantanen T, Jørgensen K B and Snieckus V 2017 Atropisomerism in tertiary biaryl 2-amides: A study of Ar-CO and Ar-Ar' rotational barriers *J. Org. Chem.* **82** 7300
- Bihlmeier A, Rotzler J, Rickhaus M, Mayor M and Kloppe W 2015 Activation enthalpies and entropies of the atropisomerization of substituted butyl-bridged biphenyls *Phys. Chem. Chem. Phys.* **17** 11165
- Perrin D D and Armarego W L F 1988 In *Purification of laboratory chemicals* 3rd edn. (London: Pergamon Press)
- Dolomanov O V, Bourhis L J, Gildea R J, Howard J A K and Puschmann H 2009 OLEX2: a complete structure solution, refinement and analysis program *J. Appl. Cryst.* **42** 339
- Burla M C, Caliandro R, Camalli M, Carrozzini B, Cascarano G L, De Caro L, Giacovazzo C, Polidori G, Siliqi D and Spagna R 2007 IL MILIONE: a suite of computer programs for crystal structure solution of proteins *J. Appl. Cryst.* **40** 609
- Bourhis L J, Dolomanov O V, Gildea R J, Howard J A K and Puschmann H 2015 The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment-Olex2 Dissected *Acta Cryst.* **A71** 59
- Nelson D J, Collado A, Manzini S, Meiries S, Slawin, A M Z, Cordes D B and Nolan S P 2014 Methoxy-functionalized N-heterocyclic carbenes *Organometallics* **33** 2048

20. (a) Tretiakov M, Shermolovich Y G, Singh A P, Samuel P P, Roesky H W, Niepötter B, Visschera A and Stalke D 2013 Lewis-base stabilized diiodine adducts with *N*-heterocyclic chalcogenamides *Dalton Trans.* **42** 12940; (b) Nelson D J, Collado A, Manzini S, Meiries S, Slawin A M Z, Cordes D B and Nolan S P Methoxy-Functionalized *N*-Heterocyclic Carbenes *Organometallics* **33** 2048 ; (c) Srinivas K, Suresh P, Babu C N, Sathyanarayana A and Prabusankar G 2015 Heavier chalcogenone complexes of bismuth(III)trihalides: Potential catalysts for acylative cleavage of cyclic ethers *RSC Adv.* **5** 15579
21. Sathyanarayana A, Srinivas K, Mandal A, Gharami S and Prabusankar G 2014 Synthesis, spectral and structural properties of bis-imidazole selones *J. Chem. Sci.* **126** 1589
22. Aldridge B, De Luca G, Edgar M, Emsley J W, Furby M I C and Webster M 1998 The structure of 2,2'-difluorobiphenyl in solid crystalline and liquid crystalline phases *Liq. Cryst.* **24** 569