



OPEN

Structural and spectroscopic characterization of N^1, N^2 -diphenylacenaphthylene-1,2-diimines and the influence of substituents on the viscosity of alkyl magnesium solutions

Julia Felicitas Schwarz & Clemens Schwarzinger[✉]

Butyl octyl magnesium solutions are important raw materials in various chemical processes but suffer from their high reactivity with even traces of water, protic solvents or oxygen and an increased viscosity in hydrocarbon solution due to the formation of polymeric structures. N^1, N^2 -diphenylacenaphthylene-1,2-diimines (BIANs) have already been identified as potential candidates to reduce the viscosity of alkyl magnesium solutions and this study provides a systematic insight into the dependence of this ability on the position and structures of substituents on the BIAN. Besides the various BIANs, $ZnCl_2$ complexes and hydrogenated derivatives were characterized and tested for their ability to reduce the viscosity. HPLC-high resolution mass spectrometry, MALDI-ToF mass spectrometry, but most important FTIR and NMR experiments under inert conditions have been used to shine light on the interaction of the different BIAN derivatives with alkyl magnesium solutions. Hydrogenated BIANs, especially those with bulky alkyl groups in the *ortho* position(s) have been identified as the most promising candidates. An additional benefit of the hydrogenated species is that in contrast to BIANs and BIAN-Zn complexes they do not undergo permanent chemical modification and can be reused after extraction.

Keywords Viscosity reduction, Magnesium alkyls, BIAN, MALDI, FTIR, HPLC-MS

In the year 1900 Victor Grignard was the first to find organomagnesium halides, which can directly be synthesized by the alkyl halide with magnesium in diethyl ether^{1,2}. These organomagnesium compounds opened a new group of powerful and versatile reagents. Organomagnesium compounds can either be dialkyl magnesium compounds (R^1-Mg-R^2) or alkyl magnesium halogenides ($R-Mg-X$), the latter so called Grignard reagent. Hereby R is an alkyl or aryl residue and X a chloride, iodide or bromide¹⁻⁴. Besides the ability to act as nucleophilic alkylating reagents^{5,6}, organomagnesium compounds find important applications in polymerizations, such as the production of polyethylene, polypropylene, polyethylene glycol⁷ and production of telomers⁸. However, dialkyl magnesium compounds are not so common as Grignard reagents, although they perform similar⁹. At that time, there was no large-scale production of these compounds. Nowadays, dialkylmagnesium compounds are produced on a commercial scale using magnesium and alkyl halides in hydrocarbon solvents^{3,9-11}. Also, magnesium alkyls are an important feedstock for the commercial manufacturing of magnesium chloride, which is used as carrier material for highly active Ziegler-Natta catalysts. The availability in solvents like hydrocarbons is a big benefit, because they are therefore free of water or ether, which would interfere with the polymerization¹²⁻¹⁵.

As Wilhelm Schlenk discovered, the structure of organomagnesium compounds is very complex and there is not only one magnesium species present¹⁶. Magnesium chloride can be precipitated in diethyl ether by addition of 1,4-dioxane. The structure of the Grignard reagent in tetrahydrofuran and diethyl ether is also not so clear, depending on the solvent, concentration, the halogen and the organic substituent the species can be monomeric,

Institute for Chemical Technology of Organic Materials, Johannes Kepler University (JKU), Altenbergerstrasse 69, 4040 Linz, Austria. ✉email: clemens.schwarzinger@jku.at

dimeric or even oligomeric¹⁶. Especially for diethyl ether the equilibrium is on the RMgX side, whereas in tetrahydrofuran it is statistically distributed between RMgX, R₂Mg and MgX₂^{1,17}.

Without solvents the magnesium alkyls (like Et₂Mg and Me₂Mg) are solid and form a polymeric linear chain structure. This results in an electron-deficient bridge as one electron pair is shared between two bonds^{5,18}. This polymeric structure represents a major problem of dialkyl magnesium compounds in hydrocarbon solvents which is their high viscosity, resulting in an significant issue in processibility^{6,19}. However, the exact structure in hydrocarbons is still not fully understood, but a polymeric type structure is most likely^{20–22}. There have been numerous attempts to investigate viscosity modifiers, such as organometallic compounds of gallium, indium or lithium²³, organoaluminium compounds²⁴ and benzene derivatives²⁵. So far, only aluminium alkyls are used commercially for the viscosity modification, but the quantity of the additive is also limited, as too much aluminium can have a poisoning effect in the further use²⁶. Thus, there is still room to find effective viscosity modifiers that allow commercially available magnesium alkyls (butyl ethyl magnesium (BEM) and butyl octyl magnesium (BOMAG) (10–20% solutions in heptane)) to be used in higher concentrations^{10,20,22}.

In our previous research, we have already demonstrated the highly successful application of nitrogen compounds such as carbodiimides and *N*¹,*N*²-diphenylacenaphthylene-1,2-diimines (BIANs)^{20,27,28}. First reports on BIAN ligands date back to the 1960s²⁹ and nowadays these ligands exhibit a large variety of applications in metal complex catalysed reactions, for example alkene hydrogenations³⁰, alkyne semi-hydrogenations³¹ and the polymerisation of ethylene³². One big advantage of BIAN ligands is that they exhibit strong electron accepting properties and their tunability of different electron properties by functionalization of the aniline^{33–35}. Furthermore, BIAN motives can undergo reduction to the corresponding diamine (BIAN-H₄)^{35,36}. As we have seen in our recent work that BIAN derivatives are very effective viscosity reducers²⁷, this present research investigates a large variety of derivatives where position and structure of substituents have been varied (R-BIAN; where R is an alkyl, dimethyl amino or chloro residue). Additionally, Zn-complexes (R-Zn) and hydrogenated R-BIAN-H₄ derivatives are tested in the ability to reduce magnesium alkyl solutions' viscosities. Various spectroscopic techniques were used to characterize all derivatives and investigate the interactions between additive and magnesium alkyl solutions under inert conditions.

Materials and methods

The magnesium alkyl butyl octyl magnesium (BOMAG) in heptane (35.6%) was provided by LANXESS Organometallics GmbH. All reactions and sample preparations with the magnesium alkyl were carried out either in the glove box (M. Braun) under nitrogen or at a Schlenk line under argon (5.0, Linde). Reagents were purchased from commercial chemical suppliers and used without further purification, except for acenaphthenequinone (see synthesis procedure). Dry diethyl ether was purified by an M. Braun Solvent Purification System SPS-7.

General synthesis procedure

The general synthesis was carried out according to the literature^{35,37,38} with minor modifications.

Purification of acenaphthenequinone

Commercially available acenaphthenequinone tends to contain significant amounts of impurities and therefore a modified purification procedure was performed. Around 10 g acenaphthenequinone were suspended in dichloromethane (1000 mL) and refluxed for 10 min. The remaining solid particles were removed by filtration through a silica plug. After removing the solvent under reduced pressure, the acenaphthenequinone was obtained as yellow crystals.

Synthesis of R-Zn complexes

In a two-neck round bottle flask 1 equivalent acenaphthenequinone and 2.5 equivalents anhydrous ZnCl₂ (Merck, 99.95%) were refluxed in glacial acetic acid (Supelco, 100%) (5 mL per mmol of acenaphthenequinone), until a clear orange solution was obtained (after approximately 10 min). Then, 2.5 equivalents of the corresponding aniline were added and kept at reflux for further 30 min. After cooling to room temperature, the precipitate was filtered off with a frit, washed three times with ice-cooled diethyl ether (Supelco, for analysis) and dried in vacuo.

For the synthesis of *N*¹,*N*²-bis-(2,6-di-isopropylphenyl)-acenaphthylene-1,2-diimine zinc(II) chloride additional toluene (technical) was added to the acetic acid before refluxing, since the product did not precipitate. After cooling to room temperature, the mixture was cooled down in a refrigerator (−5 °C) and after approximately 48 h precipitation was observed and the product further processed as described above.

Demetallation of R-Zn complexes to R-BIAN

First the demetallation agent was prepared by dissolving 12 mmol potassium oxalate (Fisher Scientific, 99%) and 1 mmol potassium carbonate in 25 mL deionized water. The respective R-BIAN-ZnCl₂ complex was suspended in dichloromethane (20 mL per mmol) and 5 mL per mmol of the demetallation agent were added. The mixture was properly shaken until all solid was dissolved. The organic phase was dried over sodium sulphate, the solvent removed and dried in vacuo.

Reduction of R-Zn complexes to R-BIAN-H₄

This synthesis was performed under inert conditions (argon) using a Schlenk line. Dry diethyl ether (25 mL) was added into a 100 mL Schlenk flask and cooled to 0 °C using an ice bath. Then, 1.5 equivalents (3.0 mmol) AlCl₃ (Acros, 98.5%) were added and the mixture stirred for 10 min. Afterwards, 9 mL of a 1 M LiAlH₄ solution (9 mmol, 4.5 equivalent, Merck, 95%) in dry diethyl ether were added and the mixture cooled to −50 °C using a

cooling bath with *iso*-propanol and liquid nitrogen. After the addition of the respective R-BIAN-ZnCl₂ complex (1 equivalent) the mixture was allowed to warm up to room temperature overnight. After that further 25 mL diethyl ether were added and the reaction slowly quenched by the dropwise addition of methanol, until the gas evolution stopped. The solvents were removed under reduced pressure, the resulting solids ground and extracted with dichloromethane (DCM, 100 mL). The suspension was filtered over celite, the filter cake washed with around 20 mL DCM and afterwards the DCM removed. The resulting product was dried in vacuo.

Viscosity reduction of alkyl magnesium compounds

To guarantee the absence of water, all additives were dried for 24 h under high vacuum (up to 10⁻⁷ mbar) and then stored in the glove box. For the viscosity modification around 5.5 g of a BOMAG solution (35.6% in heptane) were used and approximately 2.5 mol% (relative to the Mg content) additive added at room temperature. To get all additive into the reaction mixture, the flask was rinsed with a defined amount of heptane to achieve a BOMAG concentration of 30%. The mixture was stirred for at least 30 min and poorly soluble additives up to 2 h at room temperature.

Afterwards the viscosity was measured using a DV2T Brookfield spindle viscosimeter. For this purpose, 7 mL of the modified magnesium alkyl were transferred to the small sample vessel (in the Glove Box) and the measurement was then carried out under an argon stream at 21 °C with a SC4-18 spindle. The rotational speed was adjusted, depending on the viscosity.

Quenching of the modified magnesium alkyls

After the viscosity measurement the modified magnesium alkyls were diluted with approximately 10 mL heptane and water added dropwise. During the exothermic reaction, the alkyl magnesium is destroyed in a controlled manner and magnesium hydroxide is formed. The initial colours of the solutions changed once all of the magnesium alkyl had reacted. After separating the organic and aqueous phase, heptane was removed under reduced pressure. The oily, partially solid residue was dried on the high vacuum pump (10⁻⁷ mbar) for 24 h.

Analytical methods

NMR spectroscopy

¹H- and ¹³C-NMR data were collected on a Bruker Avance 300 MHz spectrometer and some time and air sensitive samples were recorded on a Bruker Avance 500 MHz spectrometer. Chemical shifts are given in ppm (parts per million) and are referenced to the residual solvent signals according to literature³⁹. For air and water sensitive compounds benzene-d₆ (deuteron, 99%) was used and for all other measurements freshly percolated CDCl₃ (Roth, 99.8%) was chosen.

HPLC-MS

The analyses were performed by reversed-phase chromatography using a Surveyor HPLC (Thermo Fisher Scientific) equipped with a Zorbax SB-C18 column (150 mm × 2.1 mm, 5 μm; Agilent). The column temperature was set to 40 °C, and the injection volume was 1 μL. Analytes were separated by gradient elution with mobile phase A containing 0.1% formic acid (FA) in water and mobile phase B containing 0.1% FA in acetonitrile at a flow rate of 0.2 mL min⁻¹. The elution gradient starting conditions were 90% A and 10% B. After 1 min, the proportion of B was linearly increased to 95% at 25 min, where it was held for further 35 min. High-resolution mass spectra were obtained using an LTQ Orbitrap Velos (Thermo Fisher Scientific), with an APCI source operated in positive ionization mode. The resolution was set to 30,000, and diisooctylphthalate (m/z = 391.2843) was used as internal standard for mass calibration. Spectra were collected from 80 to 1,000 m/z, and data were analysed using Xcalibur software (Thermo Fisher Scientific; version 2.2 SP1.48).

GC-MS

GC-MS analyses were carried out on a Trace GC/Polaris MS (Thermo Fisher Scientific). The GC column temperature conditions were as follows: initial temperature 40 °C, hold for 1 min, increase at 15 °C min⁻¹ to 300 °C, and hold this temperature for 2 min. Helium gas flow was set to 1.5 mL min⁻¹, the total split flow was 100 mL min⁻¹. Mass spectra were recorded under electron impact ionization at 70 eV electron energy in the range from m/z 15 to 350.

FTIR spectroscopy

Spectra were collected with a diamond ATR unit on an iZ10 bench attached to an iN10 MX FTIR microscope (Thermo Fisher Scientific). Resolution was set to 4 cm⁻¹, spectral range from 600 to 4000 cm⁻¹, and 32 spectra were collected and averaged, except for the experiments under argon, where only 8 scans were used. For the inert measurements a one-inch diameter polymer cylinder was placed around the diamond crystal of the ATR unit, and the setup was flushed with argon from the top during collection of background and initial spectra. The air sensitive substances were transferred to the FTIR spectrometer by an argon flushed syringe and a drop of the solution was placed directly on the top of the ATR crystal. The first spectra were recorded under a stream of argon which was then removed and further spectra collected in the presence of air.

MALDI mass spectrometry

MALDI mass spectra of the Zn-complexes and some BIANs were recorded on a Bruker UltraflexExtreme in reflectron mode using positive ionization. Sample preparation consisted of mixing the solid samples with matrix (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile, DCTP) in a ratio of approximately

5:100. Around 5000 individual spectra were recorded and summed up to achieve the final mass spectrum. Calibration was carried out with polyethylene glycol 300 and 600 using the same sample preparation protocol and identical laser power.

Results and discussion

Synthesis and characterization of BIAN derivatives

As already described in our previous work²⁷, BIANs have shown to interact with alkyl magnesium solutions and have the potential to lower their viscosities. In contrast to the past study, this time a solution of butyl octyl magnesium (BOMAG) in heptane was used as this is the commercially available product unlike the toluene solution used previously and it has a higher concentration of the alkyl magnesium compound, in this case 35% by weight. To better understand the influence of the substituents present on the basic BIAN structure, we have synthesized a series of derivatives where the type and position of the residues have been varied. As not all desired aniline moieties necessary for the synthesis were commercially available, or, in some rare cases, were simply too expensive to justify an industrial application, not all isomers were synthesized in the course of this study.

Figure 1 shows the general reaction scheme for the synthesis of BIANs and their hydrogenated analogues (R-BIAN-H₄) as well as a list of compounds used.

The reaction pathway to the BIANs proceeds via a zinc complex, which is typically not isolated. In our study we have isolated these compounds to test them for their viscosity reducing potential as well as to investigate the influence of a pre-existing complex. An additional bonus of using these compounds would be that the synthesis route is shortened by one step and thus the production costs lower.

The second group of compounds that is newly introduced in this work are hydrogenated BIANs (R-BIAN-H₄). As we have previously described²⁷, an important step in the viscosity reduction mechanism of BIANs is the formation of a complex between Mg and the C=N double bonds. During this complexation one alkyl residue is transferred onto the carbon atom of one C=N double bond and an NH group is thus formed. As those isolated reaction products have then successfully been used for further viscosity reduction and afterwards could again be isolated without further permanent chemical modification, the idea behind this approach was to investigate if a double bond is even necessary at all. Also, the influence of different substituents, e.g., alkyl groups of different bulkiness (methyl, isopropyl and *tert*-butyl), an aromatic substituent, chlorine, and one alkylamino group in terms of their ability to reduce the viscosity of BOMAG solutions was tested. Substituent positions screened were *ortho* and *para*, as well as combinations thereof.

Characterization of the synthesized BIAN derivatives was carried out by using NMR spectroscopy as well as mass spectrometry. In both cases hydrolysis of certain compounds due to contact with acidic solvents was observed, in the case of NMR the use of freshly percolated chloroform could solve all issues. For HPLC-MS analyses an acidic mobile phase was necessary, thus, decomposition could not be prevented in all cases. In the cases where no intact BIAN could be detected and for all Zn-complexes solvent free MALDI-ToF MS analysis was applied. All data on the synthesized substances including NMR and *m/z* values can be found in the SI (Figs. S1–S82).

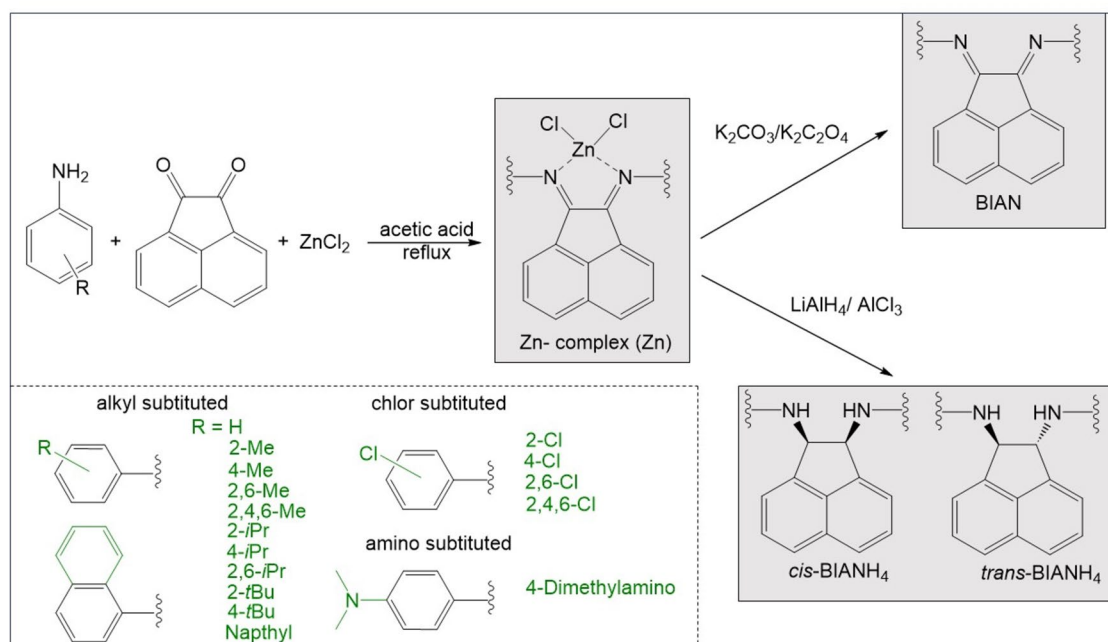


Fig. 1. General synthesis route for the manufacture of R-BIAN-Zn complexes, R-BIANs and their hydrogenated analogues (R-BIAN-H₄).

In Fig. 2 the $^1\text{H-NMR}$ spectra of 2-*i*Pr-BIAN, its Zn-complex and the hydrogenated moiety are displayed. Comparing the BIAN to the Zn-complex it can be seen that most signals are identical but shifted to a lower field in the Zn-complex, and the methyl groups of the isopropyl units are split into two signals (Fig. 2a,b). While the BIAN shows the expected doublet at 1.1 ppm (12 protons), the Zn-complex has a triplet at 1.3 ppm and an unsymmetrical quartet around 1 ppm (6 + 6 protons). This splitting suggests that the chemical surrounding is changed by the coordination of the ZnCl_2 , hence the symmetrical complex suggested in Scheme 1 must be seen as a simplification.

Upon hydrogenation we see that the newly formed CH is visible at 5.6 ppm and the NH at 4.6 ppm (Fig. 2c), the identity of the latter one being confirmed by the lack of coupling in the HSQC spectrum (SI Fig. S41). Again, the methyl groups of the isopropyl residue are split, but in this case symmetrical as expected due to the loss of planarity. The isomer formed in this reaction is predominantly the *cis* isomer.

As already stated above, when running HPLC-MS experiments it was not possible to avoid the contact with acids completely as the gradient used was composed of acetonitrile and water, each containing 0.1% formic acid. By using this gradient, we could observe three different types of results. In some cases, the BIAN formation was reversed and the corresponding aniline derivative and acenaphthoquinone were completely reformed (Fig. 3a). In other cases, partial hydrolysis took place and while aniline as well as acenaphthoquinone were formed besides a compound with only one aniline moiety cleaved off, to various extents the intact BIAN derivative was found from which the exact mass could be retrieved (Fig. 3b). The cases where no decomposition took place are rare and typically have one or two bulky groups in the *ortho* position(s) (Fig. 3c), indicating a steric hindrance of the hydrolysis (see Table 1). The Zn-complexes were all together not stable in the acidic solvent and behaved exactly the same as their corresponding BIAN analogues. The hydrogenated R-BIAN- H_4 s, on the other side, were all stable under the chosen conditions and only yielded peaks for intact moieties, sometimes two peaks with identical mass were observed indicating the formation of a second diastereomer (Fig. 3d)³⁵. A correlation between the hydrolytic stability of the BIAN derivatives and the viscosity reduction behaviour could not be found.

To successfully obtain the molecular weights of the Zn-complexes and the unstable BIANs, MALDI mass spectra were recorded. By using this technique all the Zn-complexes could be identified as their BIAN- ZnCl^+ ions, rather than the typically expected proton or alkali adducts (see SI Sect. 1). The BIANs were identified as Na^+ and K^+ adducts, the first ones were used for the determination of the molecular weights. Besides those alkali adducts, a protonated, but dehydrogenated ($\text{MH}^+ - \text{H}_2$) ion was detected for all species, except for the 2,4,6-trichloro derivative, where dehydrochlorination was observed instead.

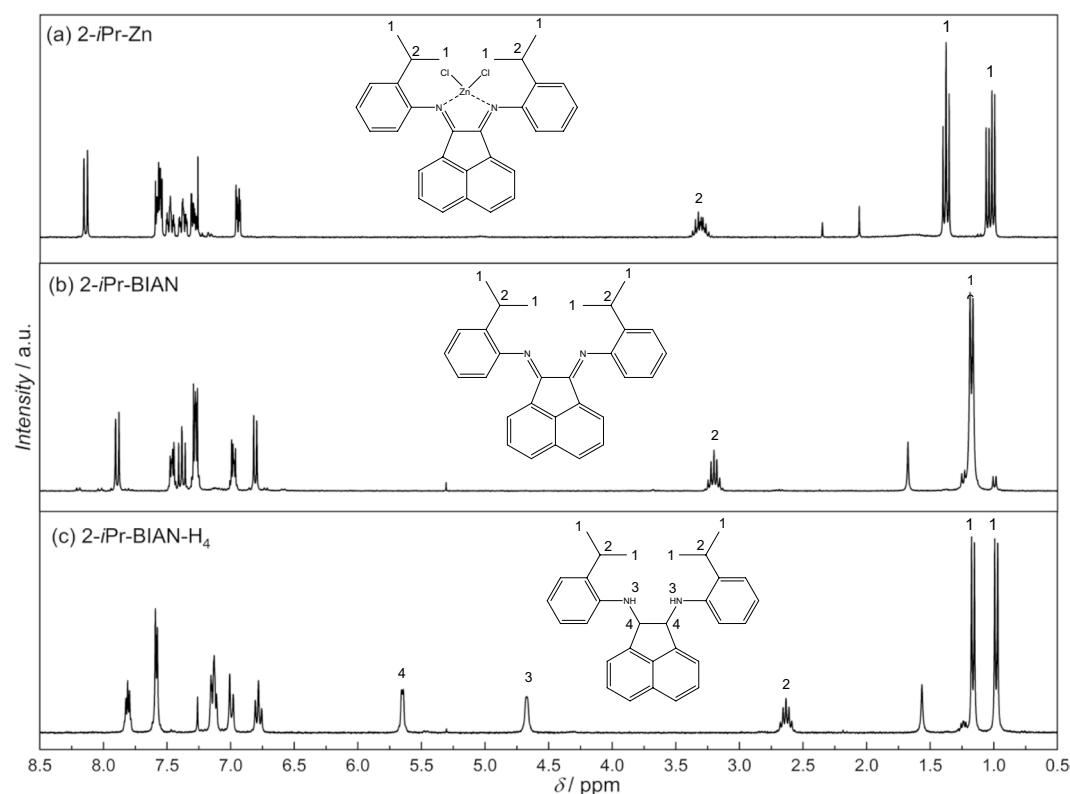


Fig. 2. $^1\text{H-NMR}$ of 2-*i*Pr-BIAN, the corresponding Zn-complex and hydrogenated BIAN. CDCl_3 @ 7.26 ppm, H_2O @ 1.6 ppm, CH_3COOH @ 2.1 ppm.

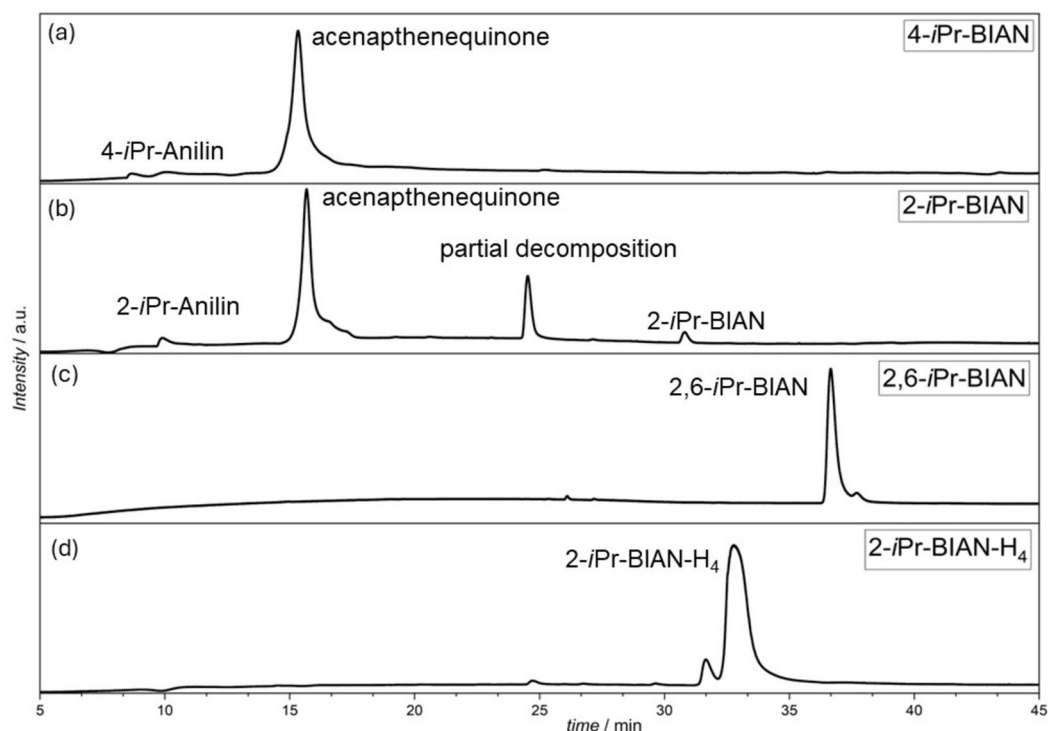


Fig. 3. HPLC–MS chromatograms of 2-*i*Pr-BIAN compounds showing different hydrolysis behaviour; (a) completely unstable 4-*i*Pr-BIAN; (b) partially stable 2-*i*Pr-BIAN; (c) fully stable 2,6-*i*Pr-BIAN; and (d) the fully stable 2-*i*Pr-BIAN- H_4 .

R	BIAN	BIAN- H_4	R	BIAN	BIAN- H_4
H	×	✓	2- <i>tert</i> Bu	✓	✓
2-Me	×	✓	4- <i>tert</i> Bu	×	✓
4-Me	×	✓	Naphthyl	~	✓
2,6-Me	~	✓	4- <i>N,N</i> -dimethylamino	×	~*
2,4,6-Me	~	✓	2-Cl	~	✓
2- <i>i</i> Pr	~	✓	4-Cl	×	✓
4- <i>i</i> Pr	×	✓	2,6-Cl	~	✓
2,6- <i>i</i> Pr	✓	✓	2,4,6-Cl	×	✓

Table 1. Hydrolysis stability of the various BIAN derivatives as observed by HPLC–MS analysis. ✓—Fully stable; ~—partially stable; ×—completely unstable (acenaphthoquinone and corresponding aniline). *Product could not be isolated.

Viscosity reduction effect of BIAN derivatives on alkyl magnesium compounds

The starting material, 35% BOMAG in heptane, has a viscosity of 137.8 ± 3.0 mPa s (average of five measurements, Table 2). At first, unmodified and unsubstituted BIAN was measured as benchmark, which already reduces the viscosity of the BOMAG solution to 39 mPa s. When trying to repeat this experiment with the Zn complex and the hydrogenated BIAN a first problem arose, which is the solubility of the BIAN derivatives in the BOMAG-heptane solution. Both derivatives were only poorly soluble, and a large amount of the modifier remained undissolved (Table 2). Nevertheless, in those cases where the compounds were not completely soluble, the saturated solutions were used for the viscosity measurements. Despite this problem, the Zn complex showed a reduction of the viscosity to 66 mPa s. The hydrogenated BIAN (H -BIAN- H_4) did not show any influence at all, and the viscosity remained constant at 140 mPa s. In general, all BIANs showed good solubility (except for the naphthyl and 2,4,6-trichloro derivative, which proved to be insoluble in all three modifications), in case of the hydrogenated products the *ortho* substituted products are better soluble than the *para* substituted ones, again with one exception which are the *tert*-butyl derivatives. For the Zn-complexes, no trend could be found.

All synthesized BIANs, Zn-complexes and BIAN- H_4 have been tested and the measured viscosities are listed in Table 2. As shown in Table 2 not all derivatives were completely soluble but no trend regarding the substituent position can be observed. For example, while the hydrogenated 2-*i*Pr is completely soluble and the 4-*i*Pr not, it is the other way round for the hydrogenated 2-*t*Bu and 4-*t*Bu. The BIANs are all, except for the 2,4,6-Cl, easily

R	Zn-complex		BIAN		BIAN-H ₄	
	η /mPa s	soluble	η /mPa s	soluble	η /mPa s	Soluble
BOMAG 137.8						
H	65.9	×	38.7	✓	140.4	×
2-Me	28.5	✓	36.3	✓	42.9	✓
			34.2			
4-Me	40.4	✓	29.5	✓	110.7	~
			29.2			
2,6-Me	73.8	×	116.4	✓	33.6	~
2,4,6-Me	46.5	✓	70.2	✓	27.3	✓
			74.7			
2- <i>i</i> Pr	29.3	~	44.7	✓	28.4	✓
4- <i>i</i> Pr	39.8	~	36.1	✓	127.8	~
2,6- <i>i</i> Pr	39.5	✓	40.8	✓	24.8	✓
2- <i>tert</i> Bu	46.7	~	77.8	✓	26.5	~
4- <i>tert</i> Bu	38.7	~	35.9	✓	123.0	✓
Naphthyl	64.3	×	54.4	×	173.6	×
<i>N,N</i> -dimethyl amino	–	–*	171.6	✓	–	–*
2-Cl	35.9	✓	69.6	✓	44.8	✓
4-Cl	51.4	✓	31.8	✓	102.4	~
2,6-Cl	160.0	×	39.3	✓	48.0	~
2,4,6-Cl	458.3	×	230.0	×	92.1	×

Table 2. Viscosity of BOMAG solutions modified using 2.5 mol% of the different additives and their solubility in the BOMAG heptane solution. ✓—Fully stable; ~—partially stable; ×—poorly soluble. *Product could not be isolated.

soluble while the Zn derivatives are in general only poorly soluble, indicating an interaction of the BOMAG solution with Zn.

A selection of the viscosities achieved using different BIAN derivatives can be seen in Fig. 4. 2,4,6-Cl-BIAN is an absolute outlier, which, despite being only poorly soluble, increases the viscosity of the solution to 230 mPa s. A possible reason may be that the compound is not pure, which is suggested by NMR and HPLC data. Such a rise in viscosity has otherwise only been observed for the hydrogenated naphthyl-BIAN (174 mPa s) and *N,N*-dimethylamino-BIAN (172 mPa s), the latter one also despite being completely soluble. A general trend is that a substituent in position 4 shows a better viscosity reduction behavior than the same substituent in position 2, which is most likely due to the steric hindrance in the latter derivatives, as has already been seen in their increased

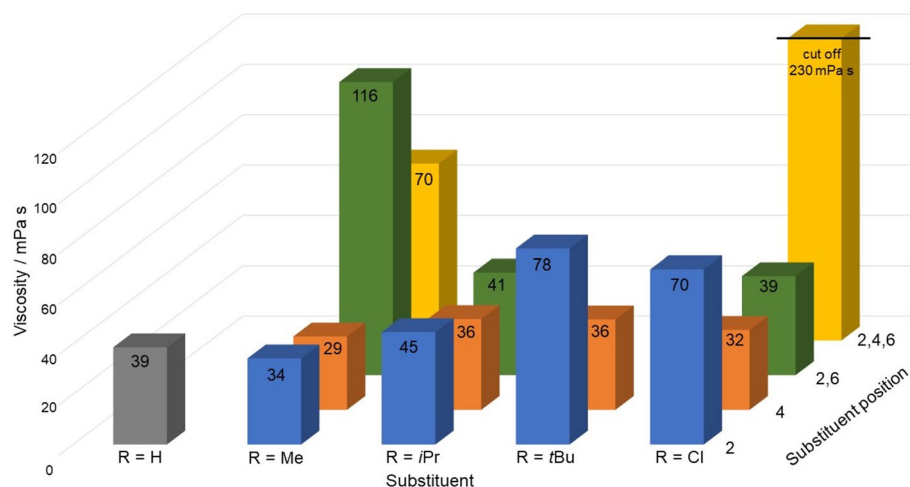


Fig. 4. Viscosity of the BIAN modified BOMAG solutions. First column shows the unsubstituted BIAN as reference. The column for 2,4,6-Cl-BIAN is cropped at 120 mPa s (would have a viscosity of 230 mPa s) for better visibility of all other compounds. Numbers written in the columns are the absolute values as listed in Table 2.

stability against hydrolysis. The viscosity of the *para*-derivatives shows a rather similar value of 29–36 mPa s, which is on the better side of all tested compounds. The 2,6-Me-BIAN has a very poor performance, while the other 2,6 derivatives give good results, even a bit better than the corresponding molecules with a single *ortho* substitution. The 2,4,6 derivatives, which were only available for methyl and chloro substituents, show very low ability to reduce the viscosity of BOMAG solutions, chlorine even increasing its viscosity as mentioned above.

When looking at the Zn complexes (Fig. 5) it can first of all be noticed that the unsubstituted H-Zn is clearly worse than its BIAN analogue (66 vs 39 mPa s), which might be due to its lower solubility (see Table 2), but also an interaction of the Zn with BOMAG. In contrast to the BIANs the viscosities of the *ortho*-isomers are a bit lower than that of the *para*-isomers, 2-*t*Bu-Zn being an outlier most likely due to its limited solubility. 2,6 and 2,4,6 isomers show the least capability to interact and break the BOMAG chains, especially the 2,6-Cl-Zn and 2,4,6-Cl-Zn compounds, but again, those derivatives could not be dissolved at 2.5 mol% and were thus tested as saturated solutions.

The most interesting results were, however, obtained with the hydrogenated BIANs. H-BIAN- H_4 (without substituents) does not show any effect on the viscosity of the BOMAG solution, the change in color, which is a first indication of complexation, is also not very pronounced (Table 3). The *para*-isomers of hydrogenated substituted BIANs all together show a very poor viscosity reduction behavior, also the 2,4,6-Cl-BIAN- H_4 derivative is rather ineffective (Fig. 6). When the substituent is located in the *ortho* position, excellent viscosity reduction behavior is observed and a trend can be seen that the larger the alkyl substituent, the better the value. This latter observation is different from the trend in BIANs and Zn complexes, where the methyl substituent works best (see Figs. 4, 5). A reason for this might be that the reaction mechanism of the latter compounds starts with the addition of an alkyl residue to the double bond and a steric hindrance would have a negative effect on this step.

When a second substituent is added in position 6 the viscosity values of around 25 mPa s can be obtained, even the 2,4,6-Me-BIAN- H_4 substituted derivative performs very well. This is comparable to the best values obtained with previously published modifiers such as bis-trimethylsilylcarbodiimide (25 mPa s), dicyclohexylcarbodiimide (41.2 mPa s), or the commercially used triethyl aluminium (20.4 mPa s)²⁰. Based on these results we conclude that for hydrogenated BIANs a steric hindrance is key to the successful reduction of the viscosity of BOMAG solutions.

To better summarize the individual trends of BIANs, Zn complexes and BIAN- H_4 compounds, we have selected all compounds where substituents in *ortho*- and *para*-positions were available and grouped them together in Fig. 7. Here, the strong difference between the *ortho*- and *para*-isomers of the hydrogenated BIANs is clearly visible, with the *ortho*-isomers being the most effective ones. But also Zn complexes and BIANs show a trend, although less pronounced. The trend within the Zn complexes is similar to the one in hydrogenated BIANs: the *ortho*-isomer is resulting in lower viscosity than the *para*-isomer, with the only exception of the 4-*t*Bu substituted derivative that is less soluble than the *ortho*-isomer. The BIANs on the other hand show the opposite trend where all *para*-isomers show a better performance than the *ortho*-isomers.

A fast way to see if any interaction between BOMAG and BIAN takes place, is the change of the solution's colour (Table 3). While the BOMAG solution is colourless, the BIAN derivatives are typically intensely coloured. When a complex is formed in solution it is indicated by a distinctive change in coloration. The BIAN compounds, especially with alkyl groups, are reddish violet in the interaction with BOMAG, whereas the Zn-complexes are mostly red in the beginning and after some minutes change to a violet colour as well. This shows the exchange of zinc with magnesium. The behaviour of chlorine substituted BIANs and their Zn derivatives is somehow different as their colour is always red. The colour of the BOMAG modified with BIAN- H_4 on the other hand differs completely. Here a yellowish colour is usually recognizable, only in very rare cases, such as with 2-*i*Pr and 4-*t*Bu, an intense blue respectively orange coloration was observed. During the careful quenching with water a

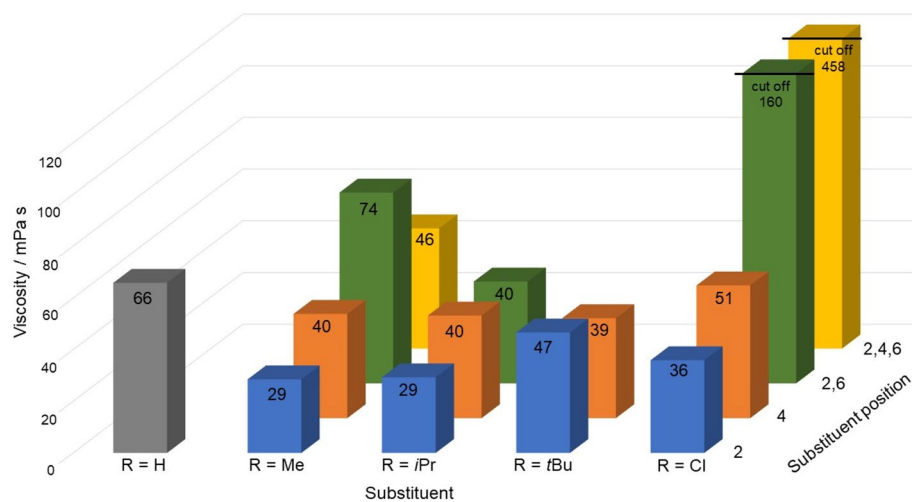


Fig. 5. Viscosity of the R-Zn complex modified BOMAG solutions. First column shows the unsubstituted H-Zn as reference. The columns for 2,4-Cl-Zn and 2,4,6-Cl-Zn are cropped at 120 mPa s for better visibility of all other compounds. Numbers written in the columns are the absolute values as listed in Table 2.

Substituent	Colour of solid	Colour BOMAG modified with BIAN	Colour gradient during quenching	Colour after quenching
Zn-complexes				
H	Yellow/green	Yellow to red	–*	Red
2-Me	Yellow	Red to violet	Orange	Red
4-Me	Orange	Red to violet	–	Red
2,6-Me	Yellow	Orange-brownish	Yellow	Red
2,4,6-Me	Red	Red to violet	–	Yellow
2- <i>i</i> Pr	Yellow	Red to violet	–	Orange
4- <i>i</i> Pr	Yellow	Red to violet	–	Red
2- <i>i</i> Pr	Orange	Red to violet	–	Yellow
2- <i>t</i> Bu	Yellow	Red to violet	–	Orange
4- <i>t</i> Bu	Orange	Red to violet	–	Red
Naphthyl	Dark red	Black	–	Orange
2-Cl	Green	Red	Orange	Red
4-Cl	Orange	Red	–	Red
2,6-Cl	Brown	Red	Violet	Colourless
2,4,6-Cl	Yellow	Red	Violet	Colourless
BIANs				
H	Orange	Red	–	Red
2-Me	Orange	Violet	–	Red
4-Me	Orange	Dark red	–	Red
2,6-Me	Orange	Violet-red	–	Orange
2,4,6-Me	Orange	Violet	–	Yellow
2- <i>i</i> Pr	Yellow	Violet	–	Red
4- <i>i</i> Pr	Orange/yellow	Violet-red	–	Red
2,6- <i>i</i> Pr	Orange	Violet	–	Yellow
2- <i>t</i> Bu	Orange	Violet-red	–	Orange
4- <i>t</i> Bu	Yellow	Violet-red	–	Red
Naphthyl	Red	Black	–	Orange
2-Cl	Red-brown	Red	–	Orange
4-Cl	Orange	Red	–	Red
2,6-Cl	Orange	Red	–	Yellow
2,4,6-Cl	Yellow	Red	–	Colourless
4-Dimethylamino	–	Black	Dark brown	Grey
BIAN-H ₄				
H	Red grey	Slightly orange	–	Yellow
2-Me	White	Yellow to greyish	Pink to green to brown to green to yellow	Green
4-Me	White	Milky yellow	Yellow to grey-green	Orange
2,6-Me	Pale red	Grey	Pink to brown to green	Yellow
2,4,6-Me	White	Green–blue	Pink to brown to green	Yellow
2- <i>i</i> Pr	White	Yellow to blue	Pink to brown to green to yellow	Orange
4- <i>i</i> Pr	White	Yellow	Green	Orange
2,6- <i>i</i> Pr	Pale yellow	Green	Orange	Yellow
2- <i>t</i> Bu	Skin coloured	Orange	–	Yellow
4- <i>t</i> Bu	White	Yellow	Green to yellow to skin coloured	Yellow
Naphthyl	Pale brown	Yellow	–	Slightly yellow
2-Cl	Grey	Yellow	–	Yellow
4-Cl	White	Yellow	–	Yellow
2,6-Cl	White	Milky yellow	–	Yellow
2,4,6-Cl	White	Milky	–	Yellow

Table 3. Colour of the solid BIAN derivatives and their colour change when interacting with BOMAG (35% in heptane). Furthermore, the colour gradient during the quenching with water and the finally achieved colour in heptane are described. *No intermediate colour observed.

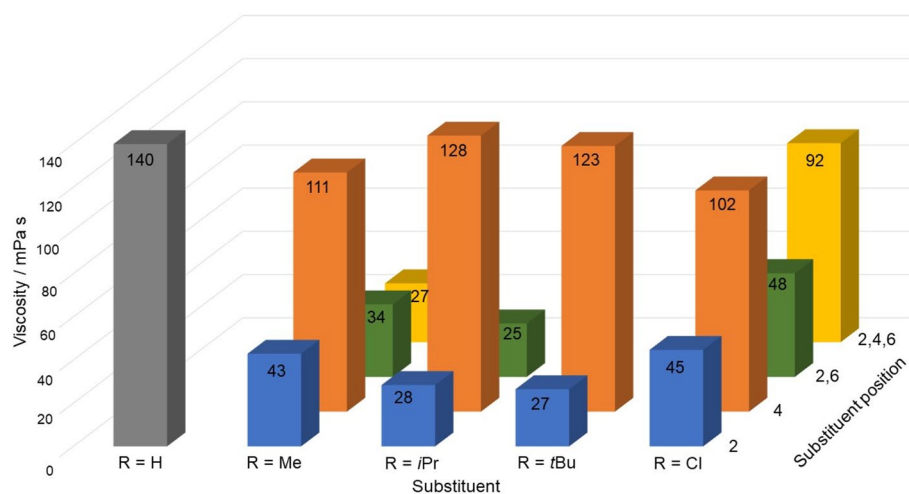


Fig. 6. Viscosity of the hydrogenated BIAN modified BOMAG solutions. First column shows the unsubstituted H-BIAN-H₄ as reference. Numbers written in the columns are the absolute values as listed in Table 2.

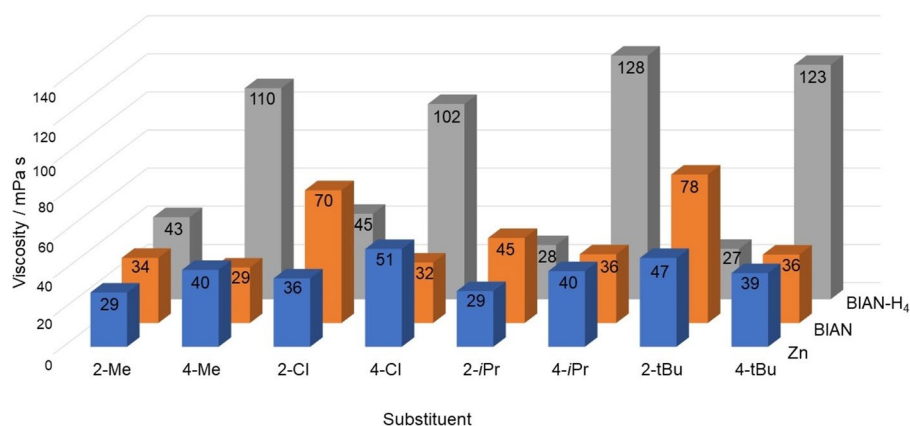


Fig. 7. Viscosity trends of *ortho*- and *para*-substituted BIAN derivatives. Numbers written in the columns are the absolute values as listed in Table 2.

colour gradient from the initial colour to pink to brown to green and finally yellow was seen for the majority of the hydrogenated derivatives.

Quenching of inert solutions

A first approach to gain insight into the mechanisms is the isolation of the BIAN derivatives after aqueous workup of the inert BOMAG-BIAN solutions. For BIANs it has already been shown that they undergo alkylation on the carbon atom of one of the C=N bonds²⁷. As expected, all BIANs were isolated as butyl or octyl substituted derivatives (SI Fig. S83) and the structures could be identified with HPLC–MS (exact masses are listed in the SI in Table S1) as well as ¹H-NMR (SI Sect. 3). The latter showed newly formed NH signals, which have unequivocally been assigned by HSQC experiments (SI Fig. S90), where no correlation of the proton signal to any carbon is found. In the case of all BIANs and their corresponding Zn-complexes the quenched products are identical, as shown in Fig. 7 for the 2-*i*Pr derivatives, and consist of a mixture of C-octyl and C-butyl BIAN as confirmed by HPLC–MS (see SI Table S1). Zn or chlorine residues could not be found in the quenched products, they are obviously transferred into the aqueous phase during quenching. A clear and quantitative assignment of the alkyl substituent from the NMR spectra could, however, not be done as those signals are obscured by other peaks in the alkyl range. Despite drying the quenched products under high vacuum for at least 12 h, we were not able to remove those impurities. Analysis of several samples with GC–MS revealed that a mixture of higher hydrocarbons and 1-octanol are present, which are derived from the industrial synthesis of the BOMAG solutions in heptane. Those impurities have not been found in our previous study²⁷, because in this case BOMAG was supplied in a toluene solution and exchanging the solvents must have led to a cleaner product. The octanol is also confirmed by ¹H-NMR, where many quenched BIANs show a triplet at around 3.7 ppm that can be assigned to

the CH₂-group of a primary alcohol (Fig. 8, SI Sect. 3). The NMR of the quenched BOMAG without any BIAN can be also seen in the SI Fig. S84.

For the quenched *para*-substituted products, the HPLC–MS measurement shows other signals in addition to the butyl and octyl signals (Table S2). Figure 9a shows the HPLC–MS of pure 2-*i*Pr-BIAN before and after quenching, where only two signals are observed, the structure with one butyl residue (36.2 min) and an octyl residue (51.4 min). These two signals can also be identified in the quenched 4-*i*Pr-BIAN (butyl residue at 34.8 min and octyl residue at 47.2 min), but additionally some smaller fragments indicating, again, a lower hydrolytic stability of the *para* isomers (Fig. 9b).

The situation with hydrogenated BIANs is of course different, as there are no more C=N double bonds available to undergo alkylation. Indeed, the hydrogenated BIANs could be regained without any structural change as could be proven by NMR as well as HPLC–MS analysis (Figs. 10, 11). HPLC–MS analysis also revealed that, in

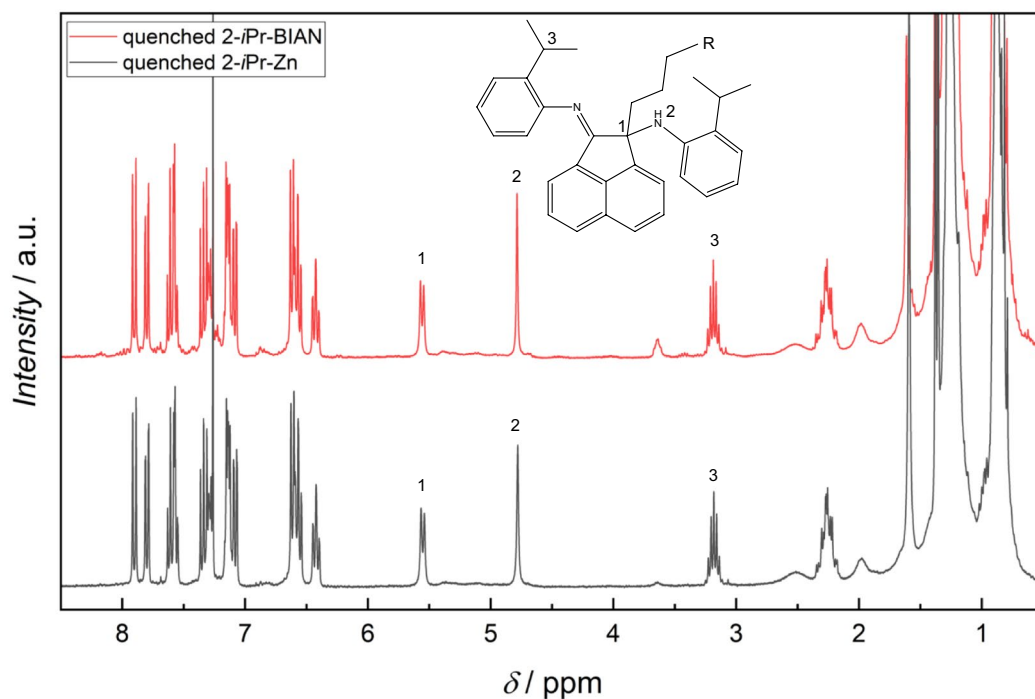


Fig. 8. ¹H-NMR spectra of the quenched 2-*i*Pr-BIAN (red) and the Zn-complex (black) being essentially similar. R = H or C₄; Octanol @ 3.6 ppm.

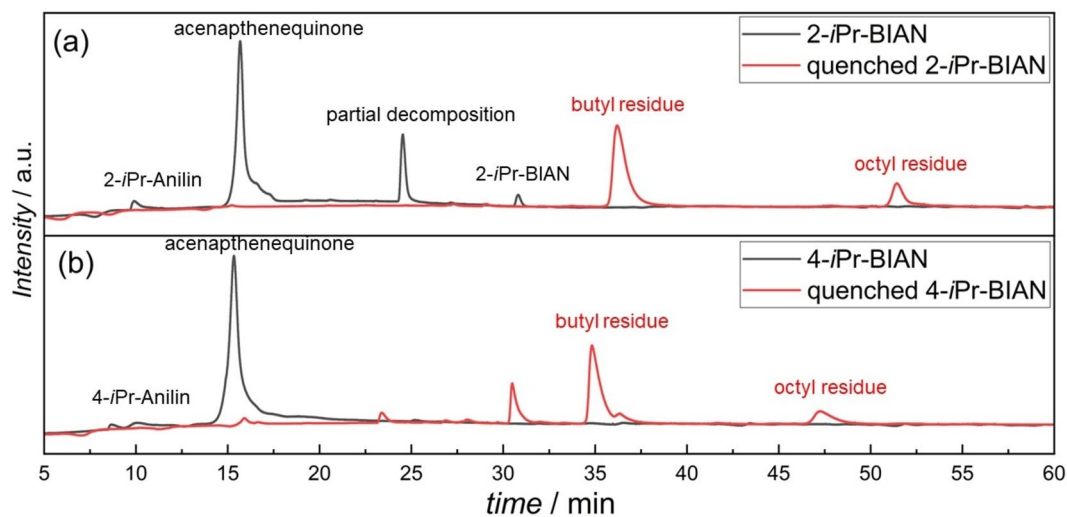


Fig. 9. Chromatograms of the initial BIAN derivatives (black) and the reaction products after quenching (red). (a) 2-*i*Pr-BIAN and (b) 4-*i*Pr-BIAN.

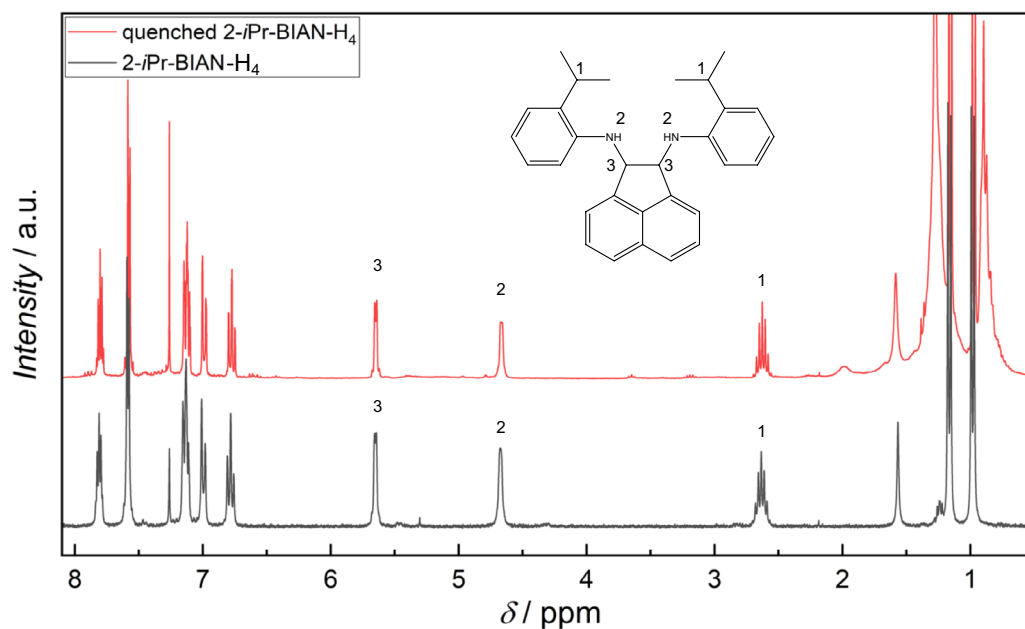


Fig. 10. ^1H -NMR spectra the hydrogenated 2-*i*Pr-BIAN- H_4 and the isolated quenched product, again being similar.

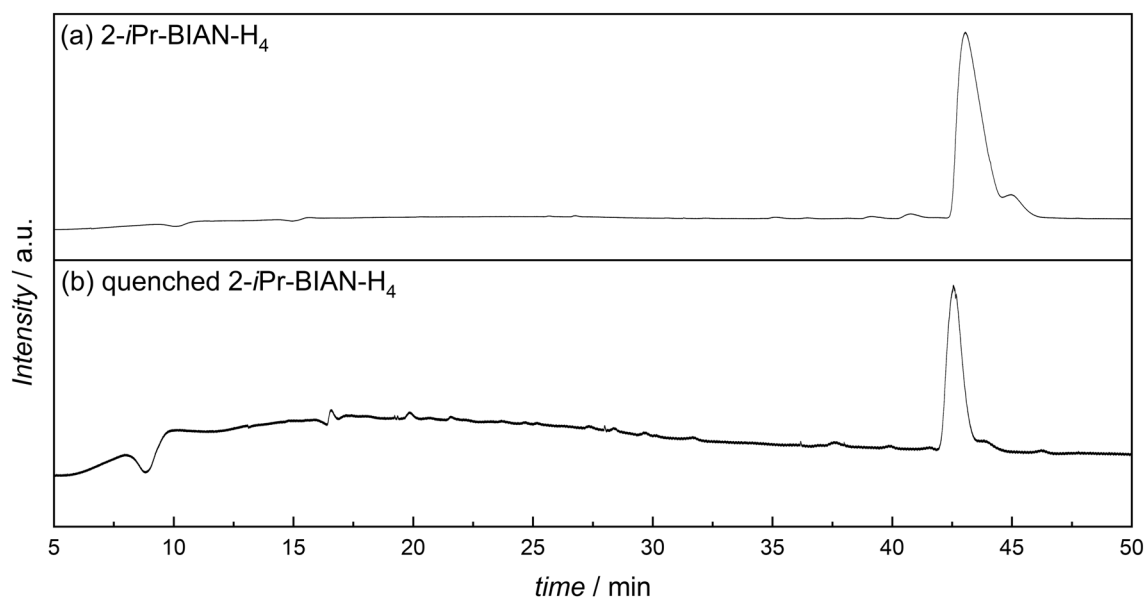


Fig. 11. Chromatograms of the hydrogenated 2-*i*Pr-BIAN- H_4 (a) and the isolated quenched product (b).

contrast to many of the BIANs and Zn complexes, the hydrogenated compounds do not undergo hydrolysis in the slightly acidic mobile phase. This behaviour sets them apart from the other derivatives as due to the lack of a chemical reaction and increased stability there is no permanent alteration of the BOMAG solution and, except for the 4-substituted derivatives, their interaction with the BOMAG chains is so strong that only small amounts are needed to reduce the viscosity of the solutions appropriately.

Investigation of the interaction with BOMAG under inert conditions

To understand the actual interaction of the BIAN derivatives with the BOMAG chains and how they are able to reduce the solution's viscosity, we have further focused on two analytical approaches. One is recording NMR spectra of inert solutions, and the other one is to observe the change of FTIR spectra of BIAN-BOMAG solutions under inert conditions and while gradually reacting with moisture until fully converted. In both cases inert conditions were obtained by shielding the solutions with argon. As a simplification, the following chapter only

discusses the results for the isopropyl BIAN derivatives and in case of the FTIR experiments the unsubstituted BIAN as reference.

FTIR analysis

To eliminate all effects and signals from the substituents we first investigated the unsubstituted BIAN. The hydrogenated form shows only a small number of well-defined bands under inert conditions, which are the aliphatic CH bonds at 2800–3000 cm^{-1} , and the aromatic CH bonds at 1600, a broad (or double) at 1450, and one at 1380 cm^{-1} (Fig. 12a).

With the ongoing reaction with moisture a major change can be ascribed to the formation of $\text{Mg}(\text{OH})_2$ leading to broad bands at 3400, 1645, and 1414 cm^{-1} . Those, together with aliphatic CH bands at 2800–3000 cm^{-1} are also the only ones seen, if pure BOMAG is left to react with moisture (SI Fig. S101).

The other change that can be observed is the evolving of the secondary NH bands at 3376 and 3408 cm^{-1} , along with a slightly better visibility of the aromatic CH bands at around 3050 cm^{-1} . The 1600 cm^{-1} band remains unchanged and the final product shows an identical spectrum as the original hydrogenated BIAN.

When comparing the inert spectra of the Zn-complex to the BIAN (Fig. 12b–d), the only difference, besides some minor changes in intensities, is that the C=N band shifts from 1640 to 1653 cm^{-1} due to complexation, as already described in literature^{40–43}. The shift is attributed to the complex of the nitrogen lone pair with a cation, in this case Zn, under inert conditions. After the reaction with moisture this band is finally shifted to 1656 cm^{-1} , which indicates that the interaction with Zn is only weak compared to Mg. Another obvious difference is that the BIAN shows an NH band at $\sim 3300 \text{ cm}^{-1}$ (this is most likely obscured by the very intense OH band in the Zn-complex). There are also two new bands evolving in the BIAN sample: one at 1500 cm^{-1} and the other at 1317 cm^{-1} . The same is seen in the Zn complex but here the bands are again obscured by the $\text{Mg}(\text{OH})_2$ bands.

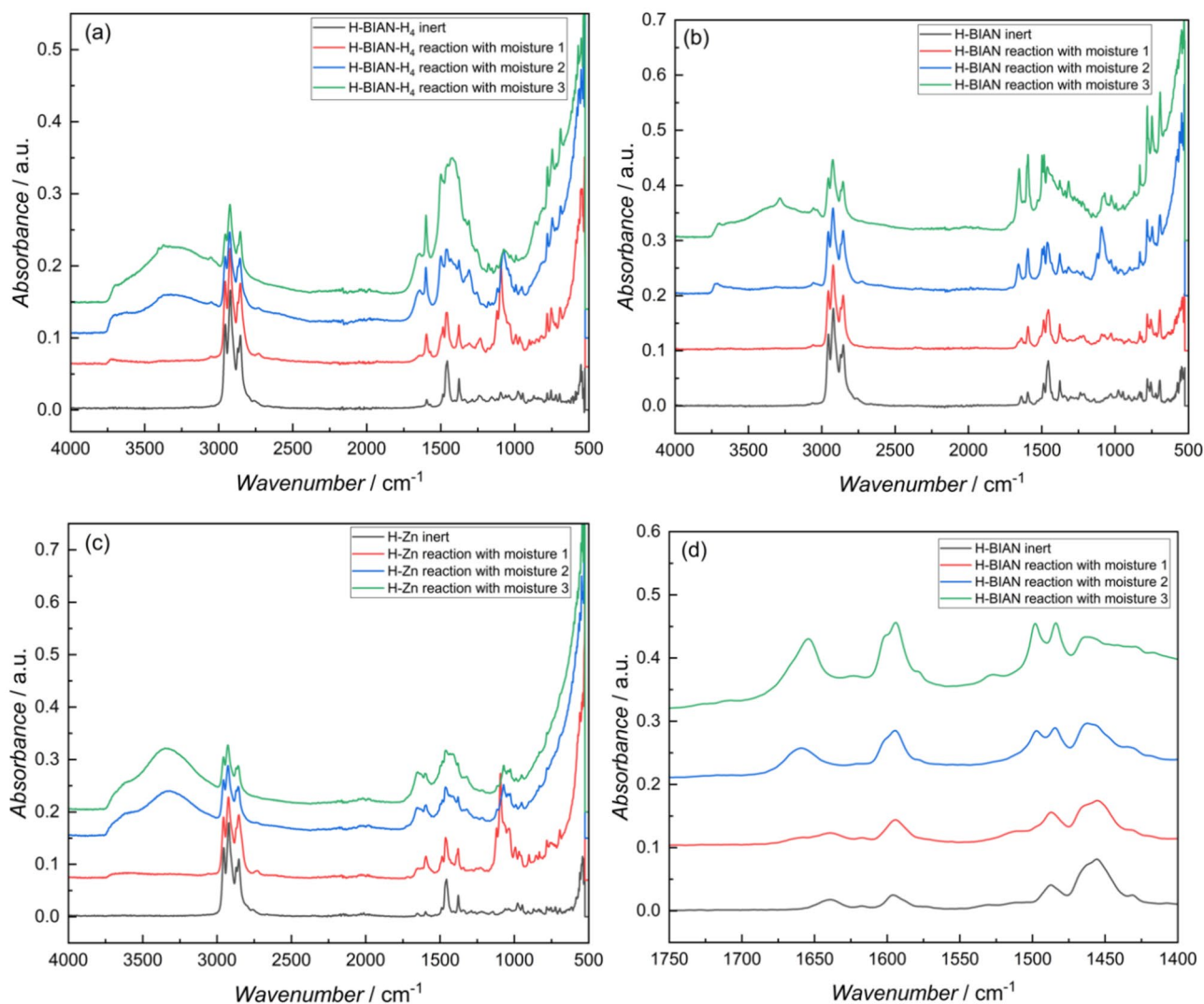


Fig. 12. FTIR spectra of inert unsubstituted BIAN derivatives in BOMAG solutions and their changes during the reaction with moisture. (a) Hydrogenated BIAN, (b) BIAN, (c) Zn-complex, (d) enlargement of the 1600 cm^{-1} region of BIAN.

The reaction products obtained after quenching the viscosity testing solutions have been analysed with FTIR spectroscopy as well and found to be identical to the ones of the final stages in the online quenching experiments.

In the next step we look at the hydrogenated BIANs with one isopropyl group attached. If this group is in the *ortho* position, the viscosity of the BOMAG solution is lowered dramatically, while when in the *para* position one of the higher values is found for hydrogenated BIANs, being in the same range as the unsubstituted BIAN. As we already know from the HPLC and NMR analyses, the hydrogenated BIAN species do not undergo any permanent reaction and after quenching can be isolated again in their native state. In this context the most obvious observation is, that, just like with the unsubstituted BIAN, in the inert spectra no NH bonds can be seen but they evolve during the reaction with water (Fig. 13). In the case of 4-*i*Pr-BIAN- H_4 a band can be seen at 3384 cm^{-1} , 2-*i*Pr-BIAN- H_4 has two bands at 3412 and 3436 cm^{-1} . For comparison, the hydrogenated 2,6-*i*Pr-BIAN- H_4 ²⁷ also shows two bands but shifted to lower wavenumbers (3340 and 3358 cm^{-1}).

In the fingerprint region, again a change in the aromatic CH band at around 1600 cm^{-1} is observed. The *ortho* isomer changes from a single band at 1595 into two bands at 1600 and 1580 cm^{-1} and the *para* isomer shows just a shift from 1607 to 1613 cm^{-1} .

An interpretation of the obtained results is that free BIANs form an intermediary complex with the Mg alkyl compounds under inert conditions as shown by the shift of the C=N band. When the Zn-complex is used, an exchange to Mg is seen as well as a reaction pathway identical to the free BIAN, both leading to singly alkylated BIANs. In contrast, the reaction pathway of the hydrogenated BIANs must be different, as no C=N double bond is present. Here, the inert IR measurements reveal that the amino group cannot be seen under inert conditions, thus the complexation with Mg must involve both amino groups. After the reaction with moisture the complex is destroyed and the initial hydrogenated BIANs are formed again.

NMR analysis

Before looking at the spectra of the inert mixtures we look again at the quenched BIAN derivatives. As already known from previous experiments²⁷, BIANs undergo addition of an alkyl group to the carbon of the C=N bond. Depending on the magnesium alkyl used, those alkyl residues may vary, in our case a mixture of butyl and octyl groups. As mentioned before, isolation of the quenched products was not straightforward, as some high boiling byproducts from the BOMAG synthesis process remain and obscure some signals in the alkyl region. In the case of all BIANs and their corresponding Zn-complexes the quenched products are identical, as shown in Fig. 8 for the 2-*i*Pr derivatives and consist of a mixture of C-octyl and C-butyl BIAN as confirmed by HPLC-MS (Fig. 8). The hydrogenated 2-*i*Pr-BIAN is not permanently changed by the BOMAG solution as can be seen by comparing the NMR spectra before and after the reaction (Fig. 10), the only difference being the alkyl signals due to the BOMAG impurities, which have been identified with GC-MS. Again, this structure was confirmed by HPLC-MS analysis (Fig. 11).

Interpretation of the NMR spectra under inert condition seems to be quite an impossible task, but as in the FTIR experiments, we recorded the spectra several times at different stages of reaction with moisture (Figs. 14, 16). Figure 14 shows the spectra of the hydrogenated 2-*i*Pr-BIAN- H_4 -BOMAG mixture starting under inert conditions, over the course of the reaction and finally the quenched product. The most obvious change is how complex the aromatic region is split up in the inert BOMAG solution, which does not allow any clean interpretation and strongly suggests the presence of multiple structures instead of a single reaction intermediate. The NH proton is seen from the beginning and does not shift very much from its starting position at 4.6 ppm until fully quenched. This is interesting in context with the FTIR spectra, where the NH bands became visible only when the sample was fully quenched. Another signal that is always clearly identifiable is the multiplet from the CH

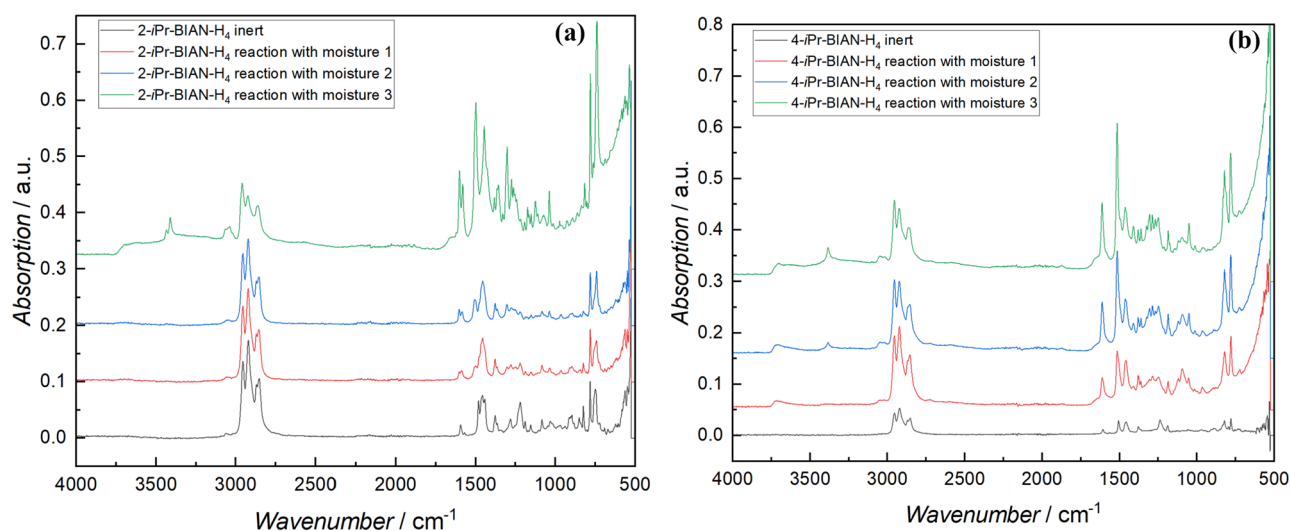


Fig. 13. FTIR spectra of (a) 2-*i*Pr-BIAN- H_4 and (b) 4-*i*Pr-BIAN- H_4 -BOMAG mixtures under inert conditions and their changes during the reaction with moisture.

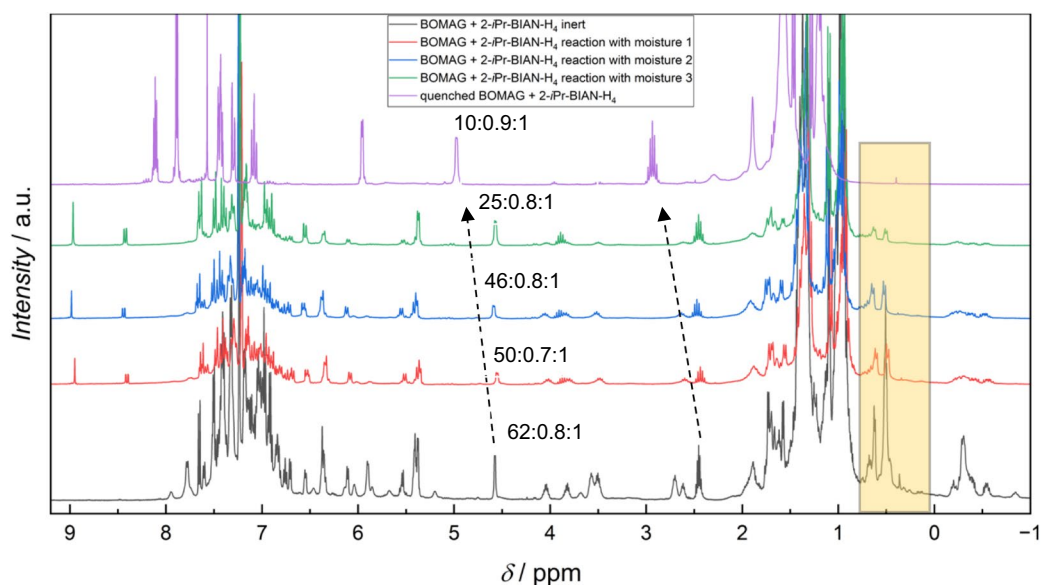


Fig. 14. ^1H -NMR spectra of the hydrogenated 2-isopropyl-BIAN with BOMAG under inert conditions (bottom), during the reaction with moisture (middle three) and the quenched product (top).

proton of the isopropyl group at 2.48 ppm, which does shift to 2.6 ppm in the quenched product. A quantitative comparison of those two signals to the combined aromatic protons and the ring CH proton reveals some interesting results. When using the isopropyl CH signal as an internal reference, the abundance of the NH signal is always slightly below 1 (as expected from such an acidic proton) but rather constant, while the total integral of the aromatic protons equals 62 in the inert state and goes gradually down to 25, until finally reaching 10 in the quenched product. The latter one is very close to the theoretical composition of 8:1:1 of the hydrogenated 2-*i*Pr-BIAN- H_4 , the difference can be explained because in our case all impurities have been included into the integral. While we cannot give a proper interpretation of this behavior so far, it supports the findings of FTIR experiments that also suggest a change in the aromatic CH bands. The ratio of NH signal to isopropyl CH signal is almost constant, which suggests that the structural integrity of the BIAN molecule is kept. Interaction of the BOMAG chains must thus mostly interfere with the aromatic structure of the BIAN, which we consider rather unlikely, or form complexes with the NH and isopropyl CH in an equimolar ratio.

A comparison of the HSQC spectra of the quenched and inert solution of the hydrogenated 2-isopropyl BIAN gives a little more insight into the inert status (Fig. 15). The alkyl region below 2 ppm in the ^1H spectra correlates well with ^{13}C signals below 40 ppm. Whilst the quenched product shows only one multiplet at 2.6/27 ppm, in the inert spectrum a series of peaks can be found with a ^{13}C shift of around 28 ppm, but in this case spread from

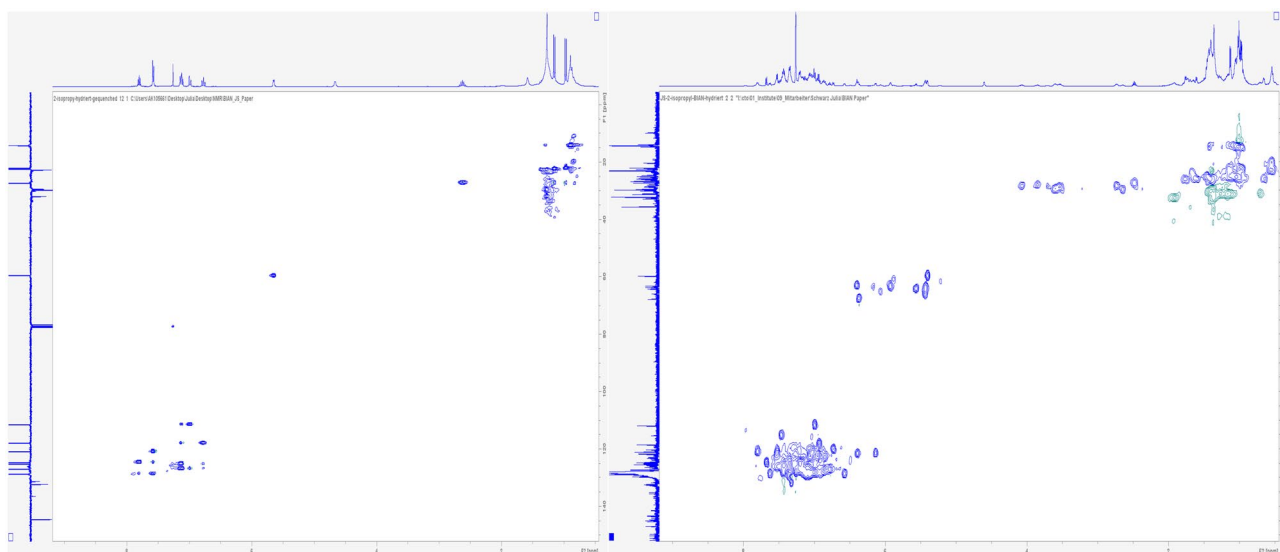


Fig. 15. HSQC spectra of the quenched hydrogenated 2-isopropyl BIAN and the inert mixture with BOMAG.

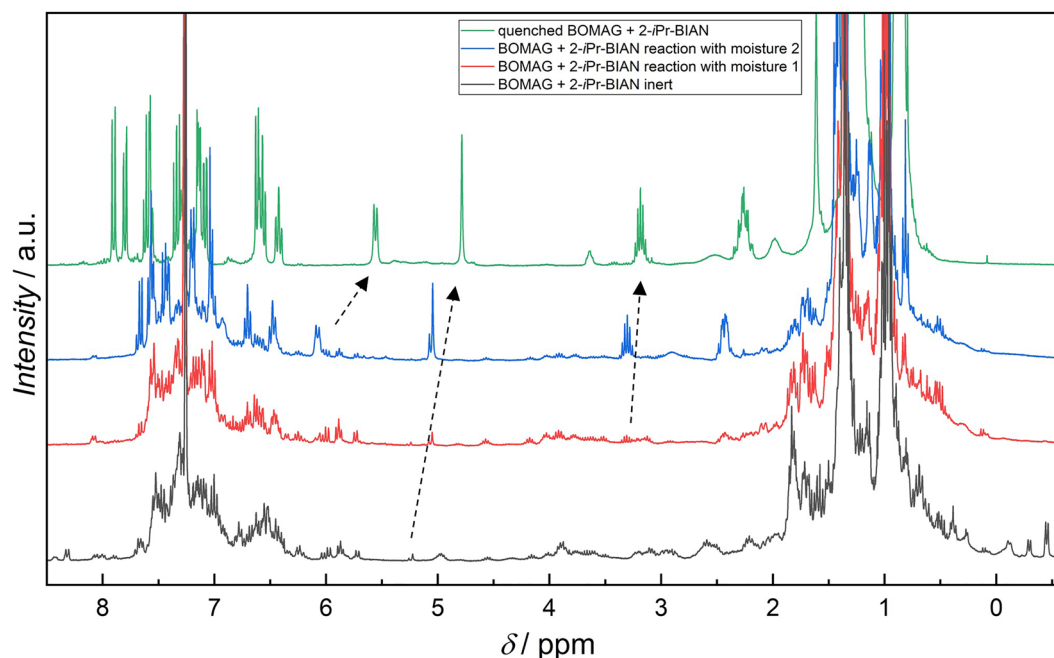


Fig. 16. ^1H -NMR spectra of the isopropyl-BIAN with BOMAG under inert conditions (bottom), during the reaction with moisture (middle two) and the quenched product (top).

2.5 to 4 ppm in the ^1H dimension. A similar situation is seen with the hydrogenated carbon atom next to the nitrogen: while there is only one clean signal at 5.6/59 ppm in the quenched product, there are at least 6 major peaks with the same ^{13}C shift in the inert spectrum. The ^1H shift of these signals now spreads between 5.4 and 6.4 ppm. Those latter signals now also interfere with some protons in the ^1H NMR spectrum that start at 6.1 ppm but have a ^{13}C shift of 120 ppm, thus identifying them as aromatic. Neither the BIAN (except for the well-defined NH and neighboring CH) nor the pure BOMAG solution show signals in this range, thus they must arise from the complexation of the two, indicating that not only one but several species are formed when hydrogenated BIANs interact with the BOMAG solution.

The situation gets even more complex when looking at the inert spectra of 2-isopropyl BIAN BOMAG mixtures and their reaction with moisture (Fig. 16). Both, the NH and the isopropyl CH cannot be clearly seen in the inert spectrum but are formed in course of the reaction. The trends that can be observed are: the NH band is shifting to a higher field, as is the adjacent CH signal. This is also seen for the isopropyl CH but to a much lesser extent.

Conclusion

In the current work we have taken a close look at the influence of substituents on N^1, N^2 -diphenylacene-1,2-diimines (BIANs) and how they influence their ability to reduce the viscosity of butyl octyl magnesium solutions in heptane. The addition of BIANs or even their precursors, the Zn-complexes results in a reduction of the BOMAG viscosity from 138 to 29 mPa s for 4-Me-BIAN and the Zn-complexes of 2-Me- and 2-*i*Pr-BIAN. While both BIANs and Zn-complexes show the same reaction pathway, starting with a permanent chemical modification—the addition of a butyl or octyl group to the carbon of the C=N double bond—their viscosity reducing behavior is different. This can be due to not yet understood interactions of Zn with the BOMAG solution.

The new class of hydrogenated BIAN- H_4 s was also utilized as viscosity reducing agents. It was found that while the 4-substituted derivatives only showed a very weak effect, the 2-substituted derivatives were extremely efficient, 2-*t*Bu-BIAN- H_4 being the best with 27 mPa s, despite being only partially soluble. The overall best results were achieved with the disubstituted 2,6-*i*Pr-BIAN- H_4 , which lowered the viscosity to below 25 mPa s. Another benefit of hydrogenated species is that they do not undergo permanent chemical modification and can be isolated and reused on the one hand, and do not consume any alkyl magnesium on the other hand. The interaction of the BIAN species with the alkyl magnesium solution was investigated by using FTIR and NMR under inert conditions and monitoring the reaction progress when slowly reacting with moisture.

We were able to show that the substitution pattern and type of substituent are important factors when BIAN derivatives are used to lower the viscosity of an alkyl magnesium solution. A reduction to 18% of the original viscosity by using 2.5 mol% of the additive was achieved which allows the processing of solutions with much higher initial alkyl magnesium load and thus an improved industrial process. Additionally, a lower consumption of inert solvents as well as a reduction in transport costs can be achieved.

But while the study has successfully identified BIAN derivatives that can be used as viscosity modifiers in industrial applications, there are still limitations in the understanding of the underlying processes. A study on

various bivalent cations might help to understand why Zn-BIANs and BIANs show different viscosity behavior. For the hydrogenated BIANs it could clearly be shown that steric hindrance is necessary to provide a good viscosity reduction agent. What has not been investigated in this study was the stereochemistry of the modifiers. While mostly the *cis* isomer is formed, sometimes *cis/trans* mixtures were obtained and used without further purification. Future experiments with stereochemically pure isomers would most likely yield even better trends in viscosity reduction.

Data availability

The datasets used and/or analysed during the current study available from the corresponding author on reasonable request.

Received: 19 April 2024; Accepted: 26 August 2024

Published online: 02 September 2024

References

- Seeger, M., Otto, W., Flick, W., Bickelhaupt, F. & Akkerman, O. S. Magnesium compounds. In *Ullmann's Encyclopedia of Industrial Chemistry* (eds Seeger, M. et al.) (Wiley, 2000).
- Mulvey, R. E. Book review of the chemistry of organomagnesium compounds, parts 1–2: R-Mg. *J. Am. Chem. Soc.* **130**(45), 15217 (2008).
- Conrad, W. K. & Jerome, F. E. *Diorganomagnesium Reagents and Methods of Preparing Same*. US19700016958;C07F3/02;C08F36/04;C07F1/00;C07F1/02(US3646231 (A)) (1970).
- Orchin, M. The Grignard reagent: Preparation, structure, and some reactions. *J. Chem. Educ.* **66**(7), 586 (1989).
- Saulys, D. A. & Hill, E. A. Beryllium & magnesium: Organometallic chemistry based in part on the article beryllium & magnesium: Organometallic Chemistry by E. Alexander Hill which appeared in the encyclopedia of inorganic chemistry. In *Encyclopedia of Inorganic and Bioinorganic Chemistry* 1st edn (ed. Scott, R. A.) (Wiley, 2012).
- Malpass, D. B., Fannin, L. W. & Sanchez, R. *Hydrocarbon Soluble Dialkylmagnesium Composition*. US19830477720;US19840583256;C07F3/02;C07F3/02(EP0119865 (A2)) (1984).
- Teruhiko, I., Naoshi, M., Seiichiro, M. & Kiyoshi, S. *Process for the Production of a High Molecular Weight Polymer of an Epoxide Using a Three Component Catalyst Comprising an Organozinc Compound, an Organomagnesium Compound and Water*. JP19630050416;JP19630056644;C08G65/12;C08G23/10;C08G23/14(US3444102 (A)) (1964).
- Kamienski, C. U. & Eastham, J. U. *Method of Preparing Telomers Utilizing as Catalysts Hydrocarbon-Soluble Organometallic Complexes of Metals of Groups I and IIa of the Periodic Table*. US19700057820;728838;C07C2/72;C07F3/02;C08F4/48;C08F36/04;C07C15/00(US3742077 (A)) (1970).
- Kamienski, C. W., Mcelroy, B. J. & Bach, R. O. *Stable Diorganomagnesium Compositions*. US19760736262;C07F3/02;C07F3/02(US4069267 (A)) (1976).
- Fannin, L. W., Malpass, D. B. & Sanchez, R. *Hydrocarbon Soluble Magnesium Compositions of High Magnesium Content*. US1979004136;C07F3/02;B01J31/12(US4207207 (A)) (1979).
- Heinz, D. C. M. K. et al. *Butyl-Octyl-Magnesium-Verbindungen*. DE19792907025;DE19792943357;C07F3/02;C07F3/02(DE2943357 (A1)) (1979).
- Forte, M. C. & Coutinho, F. M. Highly active magnesium chloride supported Ziegler-Natta catalysts with controlled morphology. *Eur. Polym. J.* **32**(2), 223–231 (1996).
- Klaue, A. et al. Insight into the synthesis process of an industrial Ziegler–Natta catalyst. *Ind. Eng. Chem. Res.* **58**(2), 886–896 (2019).
- Piovano, A. et al. Formation of highly active Ziegler–Natta catalysts clarified by a multifaceted characterization approach. *ACS Catal.* **11**(22), 13782–13796 (2021).
- Rönkkö, H.-L., Knuutila, H., Denifl, P., Leinonen, T. & Venäläinen, T. Structural studies on a solid self-supported Ziegler–Natta-type catalyst for propylene polymerization. *J. Mol. Catal. A Chem.* **278**(1–2), 127–134 (2007).
- Seyferth, D. The Grignard reagents. *Organometallics* **28**(6), 1598–1605 (2009).
- Richey, H. G. (ed.) *Grignard Reagents: New Developments* (Wiley, 2000).
- Weiss, E. Die kristallstruktur des dimethylmagnesiums. *J. Organomet. Chem.* **2**(4), 314–321 (1964).
- Malpass, D. B., Fannin, L. W. & Sanchez, R. *Organomagnesium Solutions of Low Viscosity and Process for Their Obtention*. US19800148650;DD19810231316;B01J31/00;C07F3/02;C07F3/02(EP0040141 (A1)) (1981).
- Schwarz, J. F., Holtrichter-Rößmann, T., Liedtke, C. G., Diddens, D. & Paulik, C. Modified magnesium alkyls for Ziegler–Natta catalysts. *Catalysts* **12**(9), 973 (2022).
- Ribeiro, R. et al. Deciphering the mechanism of coordinative chain transfer polymerization of ethylene using neodymocene catalysts and dialkylmagnesium. *ACS Catal.* **6**(2), 851–860 (2016).
- Hoff, R. E. (ed.) *Handbook of Transition Metal Polymerization Catalysts* (Wiley, 2010).
- Fannin, L. W., Malpass, D. B. & Sanchez, R. *Organomagnesium Solutions of Low Viscosity*. US19800148650;DD19810231316;B01J31/00;C07F3/02;C07F3/02(US4299781 (A)) (1980).
- De, V. M. N. *Process for the Preparation of a Dialkyl Magnesium Compound*. NL19690008526;C07F3/02;C07F3/02(US3737393 (A)) (1970).
- Malpass, D. B. & Webb, D. W. *Organomagnesium Solutions of Low Viscosity*. US19840591717;C07F3/02;B01J31/12;C07F3/02;C08F4/62(US4547477 (A)) (1984).
- Kamienski, C. W. & Dover, B. T. *Low Viscosity Hydrocarbon Solution of Dialkylmagnesium Compounds*. US19890391811;US19880160425;C07F3/02;C09K3/00(US5145600 (A)) (1989).
- Schwarz, J. F. et al. Structural characterization of BIAN type molecules used in viscosity reduction of alkyl magnesium solutions. *Molecules* **28**, 2 (2023).
- Holtrichter, R. T., Liedtke, C. & Schwarz, J. *Novel Organo-Magnesium Compounds and Their Use*. EP20200175740;C01F5/30;C07F3/02;C08F4/654;C10M101/00;C10M139/00;C10N10/04(WO2021233930 (A1)) (2021).
- Matei, I. & Lixandru, T. Condensation of acenaphthoquinone with primary aromatic amines in the presence of metal salts. *Bul. Inst. Politeh. Iasi.* **13**, 245–255 (1967).
- van Asselt, R. & Elsevier, C. J. Homogeneous catalytic hydrogenation of alkenes by zero-valent palladium complexes of *cis*-fixed dinitrogen ligands. *J. Mol. Catal.* **65**(3), L13–L19 (1991).
- Kluwer, A. M., Koblenz, T. S., Jonischkeit, T., Woelk, K. & Elsevier, C. J. Kinetic and spectroscopic studies of the palladium(Ar-bian)-catalyzed semi-hydrogenation of 4-octyne. *J. Am. Chem. Soc.* **127**(44), 15470–15480 (2005).
- Ittel, S. D., Johnson, L. K. & Brookhart, M. Late-metal catalysts for ethylene homo- and copolymerization. *Chem. Rev.* **100**(4), 1169–1204 (2000).
- Hasan, K. et al. Bay-region functionalisation of Ar-BIAN ligands and their use within highly absorptive cationic iridium(III) dyes. *Sci. Rep.* **7**(1), 15520 (2017).

34. Bernauer, J., Pölker, J. & von Wangelin, A. J. Redox-active BIAN-based diimine ligands in metal-catalyzed small molecule syntheses. *ChemCatChem* **14**(1), e202101182 (2022).
35. Redl, S., Timelthaler, D., Sunzenauer, P., Faust, K. & Topf, C. General access to acenaphthene-fused N-heterocyclic carbene ligands. *Organometallics* **42**(13), 1639–1648 (2023).
36. Dastgir, S., Coleman, K. S., Cowley, A. R. & Green, M. L. H. Stable crystalline annulated diaminocarbenes: Coordination with rhodium(I), iridium(I) and catalytic hydroformylation studies. *Dalton Trans.* **35**, 7203–7214 (2009).
37. Gasperini, M., Ragaini, F. & Cenini, S. Synthesis of Ar-BIAN ligands (Ar-BIAN = bis(aryl)acenaphthenequinonediimine) having strong electron-withdrawing substituents on the aryl rings and their relative coordination strength toward palladium(0) and -(II) complexes. *Organometallics* **21**(14), 2950–2957 (2002).
38. van Asselt, R., Elsevier, C. J., Smeets, W. J. J., Spek, A. L. & Benedix, R. Synthesis and characterization of rigid bidentate nitrogen ligands and some examples of coordination to divalent palladium. X-ray crystal structures of bis (p-tolylimino) acenaphthene and methylchloro [bis(o, o'-diisopropylphenyl-imino) acenaphthene] palla. *Recl. Trav. Chim. Pays-Bas* **113**(2), 88–98 (1994).
39. Fulmer, G. R. et al. NMR chemical shifts of trace impurities: Common laboratory solvents, organics, and gases in deuterated solvents relevant to the organometallic chemist. *Organometallics* **29**(9), 2176–2179 (2010).
40. Rosa, V., Avilés, T., Aullon, G., Covelo, B. & Lodeiro, C. A new bis(1-naphthylimino)acenaphthene compound and its Pd(II) and Zn(II) complexes: Synthesis, characterization, solid-state structures and density functional theory studies on the syn and anti isomers. *Inorg. Chem.* **47**(17), 7734–7744 (2008).
41. Gaballa, A. S., Asker, M. S., Barakat, A. S. & Teleb, S. M. Synthesis, characterization and biological activity of some platinum(II) complexes with Schiff bases derived from salicylaldehyde, 2-furaldehyde and phenylenediamine. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **67**(1), 114–121 (2007).
42. Caro, C. A. et al. Preparation, spectroscopic, and electrochemical characterization of metal(II) complexes with Schiff base ligands derived from chitosan: Correlations of redox potentials with Hammett parameters. *J. Coord. Chem.* **67**(23–24), 4114–4124 (2014).
43. Aranha, P. E., dos Santos, M. P., Romera, S. & Dockal, E. R. Synthesis, characterization, and spectroscopic studies of tetradentate Schiff base chromium(III) complexes. *Polyhedron* **26**(7), 1373–1382 (2007).

Acknowledgements

The authors would like to thank their students for the synthesis of several BIAN derivatives and the Institute for Catalysis at the Johannes Kepler University Linz for their support. The used NMR spectrometers were acquired in collaboration with the University of South Bohemia (CZ), with financial support from the European Union, through the EFRE INTERREG IV ETC-AT-CZ program (project M00146, “RERI-uasb”).

Author contributions

JS and CS have both equally contributed to all parts of the research and writing of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1038/s41598-024-71155-2>.

Correspondence and requests for materials should be addressed to C.S.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License, which permits any non-commercial use, sharing, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if you modified the licensed material. You do not have permission under this licence to share adapted material derived from this article or parts of it. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by-nc-nd/4.0/>.

© The Author(s) 2024