UC San Diego
UC San Diego Previously Published Works

Title
Lewis acid-base interactions enhance explosives sensing in silacycle polymers

Permalink
https://escholarship.org/uc/item/1xm539dj

Journal
Analytical and Bioanalytical Chemistry, 395(2)

ISSN
1618-2642

Authors
Sanchez, JC
Dipasquale, AG
Mrse, AA
et al.

Publication Date
2009-09-01

DOI
10.1007/s00216-009-2846-1

Peer reviewed

ORIGINAL PAPER

Lewis acid–base interactions enhance explosives sensing in silacycle polymers

Jason C. Sanchez · Antonio G. DiPasquale ·
Anthony A. Mrse · William C. Trogler

Abstract The high sensitivity of silole- and silafluorene-containing polymers for detecting organic nitro, nitrate, and nitramine explosives cannot be solely attributed to favorable analyte–polymer hydrophobic interactions and amplified fluorescence quenching due to delocalization along the polymer chain. The Lewis acidity of silicon in conjugated poly(silafluorene-vinylene)s is shown to be important. This was established by examining the ^{29}Si NMR chemical shifts (Δ) for the model trimer fragment of the polymer CH_3–silafluorene–($trans$-C_2H_2)–silafluorene–($trans$-C_2H_2)–silafluorene–CH_3. The peripheral and central silicon resonances are up-field from a TMS reference at −9.50 and −18.9 ppm, respectively. Both resonances shift down-field in the presence of donor analytes and the observed shifts (0 to 1 ppm) correlate with the basicity of a variety of added Lewis bases, including TNT. The most basic analyte studied was acetonitrile and an association constant (K_a) of 0.12 M^{-1} was calculated its binding to the peripheral silicon centers using the Scatchard method. Spin-lattice relaxation times (T_1) of 5.86(3) and 4.83(4) s were measured for the methyl protons of acetonitrile in benzene-d_6 at 20 °C in the absence and presence of the silafluorene trimer, respectively. The significant change in T_1 values further supports a binding event between acetonitrile and the silafluorene trimer. These studies as

well as significant changes and shifts observed in the characteristic UV–Vis absorption of the silafluorene group support an important role for the Lewis acid character of Si in polymer sensors that incorporate strained silacycles. The nitro groups of high explosives may act as weak Lewis-base donors to silacycles. This provides a donor–acceptor interaction that may be crucial for orienting the explosive analyte in the polymer film to provide an efficient pathway for inner-sphere electron transfer during the electron-transfer quenching process.

Introduction

Fluorescent chemosensory materials are one option for the detection of high explosives [1, 2]. They usually show good sensitivity toward volatile nitroaromatic explosives, such as 2,4,6-trinitrotoluene (TNT), and have the potential to operate in low-cost portable devices. Other explosive analytes, which include the military and civilian high explosives—HMX, RDX, and PETN, have higher lying excited states and are generally more difficult to sense. They have been detected with blue-emitting fluorescent polymers [3]. Polymeric luminescent materials containing conjugated organic frameworks take advantage of an amplified fluorescence quenching mechanism to increase detection sensitivity [4]. A key factor, among others, in the design of these polymeric materials is the inclusion of binding sites or porous pockets for effective sensor-to-analyte hydrophobic interactions. This can optimize analyte–polymer interactions and reduce energy barriers required for the excited-state electron-transfer process,
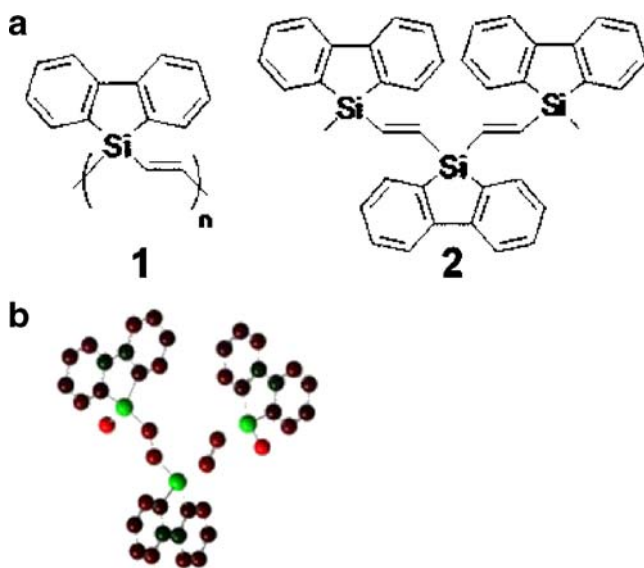
J. C. Sanchez · A. G. DiPasquale · A. A. Mrse ·
W. C. Trogler (✉)
Department of Chemistry and Biochemistry,
University of California,
San Diego, CA, USA
e-mail: wtrogler@ucsd.edu

thereby increasing the probability and efficiency of analyte detection. Swager et al. have developed rigid pentiptycene polymers that are porous in their solid-state thin films [5]. Porous films allow for ready access of highly volatile nitroaromatic explosives into the polymer structure. Adsorption is facilitated by hydrophobic π–π interactions. To further improve detection, other functionalities were employed to increase analyte binding [6]. The high sensitivity of detection has led to application of conjugated organic polymers in a commercial instrument for the detection of landmines by ICX Technologies.

We recently synthesized a conjugated silafluorene-vinylene polymer (1) and its model trimer complex (2) for explosives detection applications (Fig. 1a) [7]. In their thin films, these materials are highly luminescent in the UV-blue region of the spectrum. By targeting explosive particulates using a surface-detection method, these polymers were able to image a range of high explosives at picogram levels of sensitivity, including explosives of extreme low volatility, such as RDX and PETN. Trace detection of explosive particles is potentially important for forensic applications, such as locating areas where high explosives may have been assembled into improvised bombs. Currently, canine detection is the most widely used method for such applications, but portable trace detection approaches could be used in such applications. The silafluorene-containing polymer simultaneously detects multiple classes of explosives including nitroaromatic (TNT), nitramine (RDX), and nitrate esters (PETN) [7–10]. The relative sensitivity for detection correlates well with the energy of the lowest unoccupied molecular orbital (LUMO) of many explosive analytes [7]. The electrostatic potential (Mulliken charges) distribution calculated for the silafluorene trimer 2 reveals a positive charge density centered on the silicon atoms (Fig. 1b). This, in combination with the sensitive explosives detection results obtained for a wide range of silacycle polymers [7–15], suggested that specific sensor-to-analyte interactions might occur between these polymers and the targeted explosives.

The main difference between 1 and conjugated organic polymers used for explosives detection is the incorporation of a silacycle moiety into the polymer backbone. The silicon atoms are part of a silacyclopentadiene unit which is responsible for the unique σ*–π/π* conjugation that defines their reduced bandgap energies [16, 17]. These silacycles in dimeric and trimeric model compounds for the polymers have been characterized by X-ray crystallography and show strained internal angles near 90° at the silicon atom [7, 10, 18]. Silacycles have previously found success as effective Lewis acid catalysts [19]. When exposed to ring strain, the silicon center may expand its valence shell to act as a Lewis-base binding site via a process labeled "strain release" Lewis acidity [20–22]. This raises the possibility that the hard Lewis acid silicon center may actively bind hard weakly basic oxygen atoms in the nitro or nitrate groups of organic high explosives. It is important to understand all the factors which control detection sensitivity. In the development of a spray-on reagent for explosives detection, efficiency, cost of synthesis, and minimizing the amount of polymer reagent needed are all important practical considerations.

Experimental

General Caution: TNT is a high explosive and should be handled only in small quantities. All synthetic manipulations were carried out under an atmosphere of dry argon gas using standard Schlenk techniques. Dry solvents were purchased from Aldrich Chemical Co. Inc. and used after purification with an MBraun Auto Solvent Purification System. Spectroscopic grade toluene from Fisher Scientific was used for the fluorescence measurements. Reagents were purchased from Aldrich Chemical Co. and used as received. DNT were purchased from Aldrich Chemical Co. and recrystallized from methanol. TNT was prepared from DNT and recrystallized from toluene [15]. UV–Vis spectra were obtained with the use of a Hewlett-Packard 8452A diode array spectrometer.
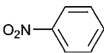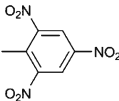
Silicon NMR measurements NMR data were collected using a Varian Mercury Plus spectrometer and a 9.4-T superconducting magnet (399.911 MHz for ^{1}H and

Fig. 1 **a** Chemical structure of poly(silafluorene-vinylene) (**1**) and methylsilafluorene-vinylene trimer (**2**); **b** Electrostatic potentials for **2** calculated using DFT at the B3LYP/6-31G* level of theory. Colors range from −0.668 to +0.668 with green denoting the electron-deficient regions and red denoting the electron-rich regions

79.450 MHz for ^{29}Si NMR). The solution-state ^{29}Si NMR spectra were recorded using an internal tetramethylsilane (TMS) reference, separated from the sample matrix using a tapered glass insert (Wilmad part WGS-5BL.) Chemical shifts were measured relative to the TMS reference (0 ppm) in all cases. ^{29}Si NMR spectra were acquired using proton decoupling during the acquisition period only. The pulse delay was set 5 s and a pulse time of 7.5 µs was used ($\pi/2$ was measured as 14 µs for **2** in benzene-d_6.) T_1 was not measured for any of the ^{29}Si sites. Typical acquisition times were 3 h. 1 Hz of exponential line broadening was applied to the data during processing. ^{1}H T_1 measurements were performed on samples using an inversion-recovery pulse sequence and VNMR-native processing algorithms. Data for T_1 analysis were taken at 20 °C in benzene-d_6. The ^{29}Si NMR data were fitted using the Lorentz equation in Origin8 (purchased from OriginLab):

$$y = y_0 + \left[(2A/\pi) \left(w \middle/ \left(4(x - x_c)^2 + w^2 \right) \right) \right]$$

Table 1 lists changes in ^{29}Si NMR chemical shifts (Δ) for both the central and peripheral silicon resonances of **2** in the presence of the Lewis-base analytes. The changes in shifts are reported from single Lorentzian fits to the NMR data using the Simplex algorithms available in Origin 8.

Table 1 ^{29}Si NMR results

Analyte	Structure	Lewis basicity $-\Delta H^\circ_{BF3}$ (kJ mol^{-1})	$\Delta_{\text{outer Si}}$ (ppm)	$\Delta_{\text{inner Si}}$ (ppm)
NB	O_2N—	35.79	0.028(1)	0.080(3)
TNT	O_2N—, —NO_2, O_2N—	—	0.103(1)	0.133(2)
ACE		76.03	0.375(2)	0.466(4)
NM	—NO_2	37.63	0.564(4)	0.517(4)
DMSO		105.3	0.613(2)	0.688(4)
THF		90.40	0.630(3)	0.687(5)
ACN	≡N	60.39	0.797(1)	0.383(4)

Spectra taken in benzene-d_6 with 27 equivalents of analyte

^{29}Si NMR spectra of the vinylene trimer (**2**) in various solvents may be found in the ESI.

Results and discussion

The nitro groups on the periphery of common explosive materials, such as TNT, have the potential to act as Lewis-base donors. It may be hypothesized that the silicon centers in the silole- and silafluorene-based polymers bind the nitro group of explosives, through the lone pairs of the nitro groups. In trace-explosive particle imaging, a dilute solution of polymer is sprayed on the sampling surface. Dissolution and mixing of explosive and polymer occurs as the film dries. Analyte–polymer acid–base interactions can provide a bridging bond through which electron transfer occurs from the excited state of the polymer to the explosive analyte. This helps explain the low detection limits observed (nanogram to picogram) and the general effectiveness of all studied silole and silafluorene polymers in detecting organic nitro, nitrate ester, and nitramine explosives using the spray-on-polymer detection method [7–15].

^{29}Si NMR spectroscopy is a technique ideally suited to identify the possible substrate/analyte interactions through the use of NMR observable parameters, such as chemical shift and relaxation time [23–27]. The model trimer complex (**2**), which proved successful as a chemosensory material for a wide range of explosives in our previous study, provides a well-characterized structural fragment of polymer **1** [10]. A series of Lewis-base analytes were chosen to span a range of basicities. The analytes include dimethylsulfoxide (DMSO), nitrobenzene (NB), nitromethane (NM), acetonitrile (ACN), acetone (ACE), tetrahydrofuran (THF) and 2,4,6-trinitrotoluene (TNT). The chemical structure and Lewis basicities for these analytes, referenced to BF$_3$ as the Lewis acid [28], are found in Table 1. Nitromethane was used as a model for aliphatic-based nitro/nitrate explosives such as RDX and PETN. Nitrobenzene and TNT represent aromatic based nitro explosives.

The ^{29}Si NMR of **2** reveals two peaks that correspond to the peripheral silicon centers and the single central silicon center of **2** (see ESI). These peaks are up-field from the TMS resonance at −9.50 ppm and −18.9 ppm, respectively. Figure 2 shows the ^{29}Si NMR spectra acquired in benzene-d_6 expanded around the resonance observed for the peripheral silicon centers of **2** with and without the addition of analytes. All spectra were acquired using ^{1}H decoupling during acquisition only and were referenced to TMS (tetramethylsilane) at 0 ppm. TMS, itself a weak Lewis acid, was contained in an internal capillary to prevent any possible interaction with the basic analytes. The observed
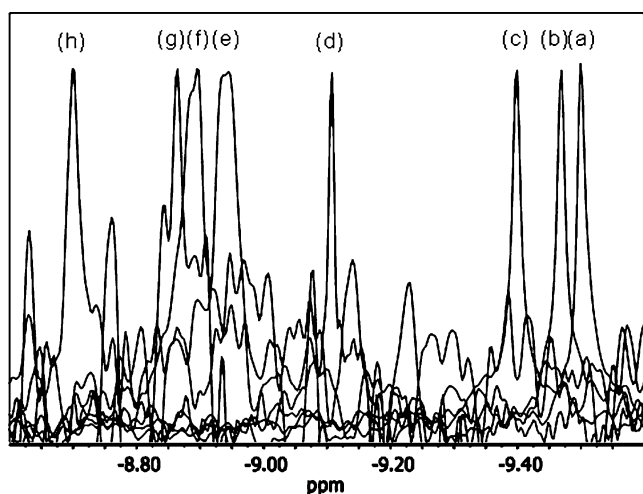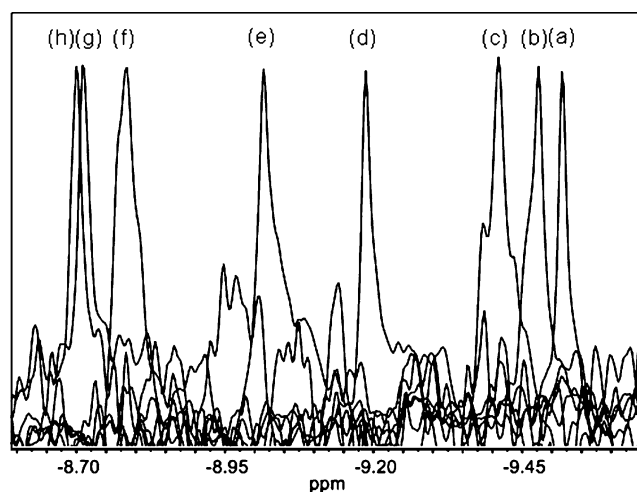
Fig. 2 ^{29}Si NMR chemical shifts for the outer Si atoms of 2 at 20 °C when exposed to 33 equivalents of a no analyte; b NB; c TNT; d; ACE; e NM; f DMSO; g THF; h ACN. Spectra were taken in benzene-d_6 solvent

Fig. 3 Superimposed ^{29}Si NMR spectra of the outer Si atoms in 2 when exposed to increasing equivalents of acetonitrile at 20 °C. a No acetonitrile; b three equivalents; c nine equivalents; d 15 equivalents; e 21 equivalents; f 27 equivalents; g 33 equivalents; h 39 equivalents

shifts are down-field and lie within a range of ~1 ppm. This finding is consistent with previous ^{29}Si NMR studies analyzing Lewis-base displacement in rigid-rod silane polymers [29].

Distinct shifts (Table 1) occur in the ^{29}Si NMR resonances for both the silicon centers of 2 when exposed to TNT. This supports the hypothesis that nitro- and nitrate-containing organic explosives can bind to these silicon-containing polymers. This weak donor–acceptor interaction could provide an efficient pathway for electron-transfer quenching of the fluorescent excited state of silacycle containing polymers.

While a general correlation is observed between Lewis basicity and the Si chemical shift with added NB, ACE, DMSO, and THF (see ESI), the data obtained for NM and ACN indicate that the correlation may be complicated by additional effects. ACN is the least-sterically restricted base and may have better access to the Si centers. This could explain the largest shift difference (Δ) of 0.797(1) ppm noticed for this analyte. In addition, ACN is the only Lewis base in this study with nitrogen donor lone pairs.

Evidence of Lewis acid–base interactions in these strained silacycle systems can also be seen through analyte titration. Figure 3 shows the chemical shifts for the peripheral silicon of 2 when exposed to increasing equivalents of ACN. The ^{29}Si NMR resonance shifts continually down-field on addition of ACN until a threshold is reached at around 33 added equivalents. An association constant (K_a) of 0.12 M^{-1} was calculated for the binding of ACN to the peripheral silicon centers of 2 using the Scatchard method [30–32]. ACN shows the largest effect on the ^{29}Si NMR resonances, providing an upper

limit for K_a in this study. Further support of substrate/analyte binding was revealed though NMR relaxation studies. Spin-lattice relaxation times (T_1) of 5.86(3) s and 4.83(4) s were measured for ACN by ^{1}H NMR in benzene-
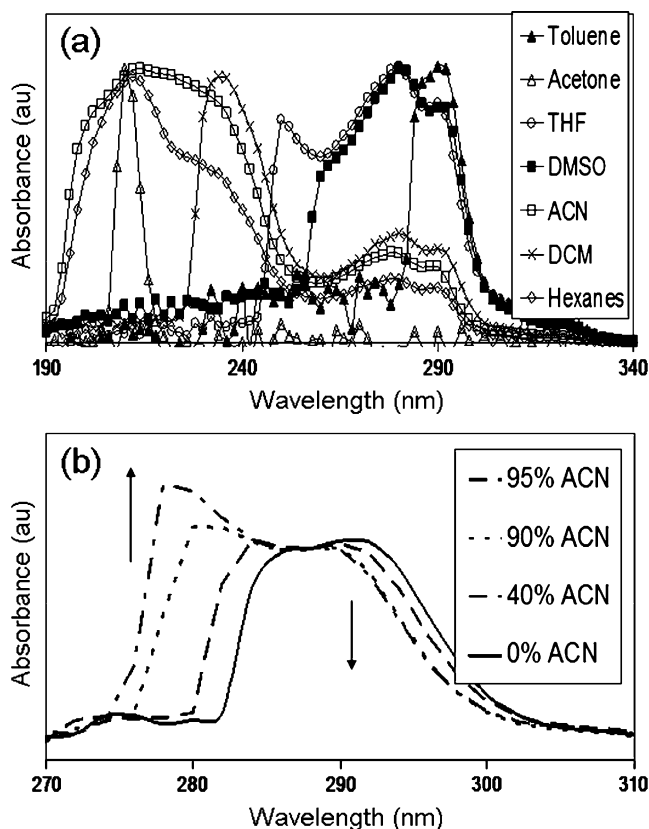
Fig. 4 UV–Vis spectra of 2. a Spectra individually taken in 100% of given solvent. DCM = dichloromethane; b spectra taken in toluene with increasing percentages of ACN

d_6 at 20 °C in the absence and presence of **2**, respectively. The significant change in T_1 values indicates a binding event between ACN and **2** [31, 33, 34]. The measured viscosity of both solutions at 20 °C were identical (0.688(3) cP), indicating no major change occurred in the solution properties affecting T_1.

Low temperature studies were performed with the intent to observe isolated populations of bound and unbound states. However, these studies were complicated by precipitation and the limiting physical properties of the solvents and analytes used. Binding studies were carried out in dichloromethane-d_2 to determine the extent that ring current effects perturb the chemical shift at silicon in toluene solvent. The peaks shift for 33 equivalents of acetone in dichloromethane-d_2 lowered to 0.270(6) ppm from 0.307(1) ppm in toluene-d_8 at room temperature and to 0.248(1) ppm from 0.436(1) ppm in toluene-d_8 at −50 °C, indicating a small but observable solvent effect with a small temperature dependence.

Binding of an analyte to the silicon center of these fluorescent molecules might also be expected to cause a change in the absorption spectra, since the lowest excited state involves excitation to the π* orbital of the metallole ring [7, 10, 15]. UV–Vis spectra were measured in a range of basic solvents. Several solvents used in the ^{29}Si NMR study (i.e., NM and NB) could not be investigated due to their strong UV absorption. Figure 4a shows the spectra of the silafluorene trimer in a variety of solvents. It is evident that the solvent has a distinct effect on the absorption properties of the silafluorene trimer. For example, the spectra reveal a blue shift in the absorption maximum (λ_{max}) of 80, 56, and 12 nm for ACN, dichloromethane (DCM), and DMSO, respectively. The isosbestic point obtained on addition of UV-transparent ACN (Fig. 4b) further suggests an equilibrium binding process that is very low, since saturation and a limiting spectrum is not obtained. The UV spectra of **2** in DMSO (dielectric constant=47) and THF (dielectric constant=7.6) are found to be very similar. This suggests that solvatochromism is not a major contributing factor to the spectral changes observed.

Conclusions

Using ^{29}Si NMR as a probe for sensor-to-analyte interactions between silafluorene-containing materials and explosive analytes, it has been shown that lone pairs on both oxygen and nitrogen atoms can bind to the silicon centers through a Lewis acid–base interaction enhanced by the ring strain in the silacycle. Further evidence for these binding events was provided by spin-lattice relaxation times and UV–Vis spectroscopy. This suggests that a fifth factor can be added to the list of metrics used to influence the ability to detect explosives with fluorescent polymers:

1. Exciton delocalization along the conjugated polymer chain leads to amplified fluorescence quenching and improves sensitivity [1].
2. Hydrophobicity and polymer porosity may enhance selective binding of organic high explosive analytes, which can be further enhanced in molecularly imprinted polymers [5, 35].
3. The polymer excited state energy is crucial in determining the range of explosives detected and the relative sensitivities of detection [7].
4. Maximizing luminescence quantum yields for emission in spectral regions easily visualized by the eye are critical to improving the sensitivity of visual imaging approaches [8].
5. Incorporating hard Lewis acid centers in a delocalized polymer chain, which are strongly coupled with the fluorescent chromophore, may further enhance explosive analyte binding and provide a facile pathway for inner-sphere electron transfer to improve both sensor selectivity and sensitivity to detection by the electron-transfer quenching process.

References

1. McQuade DT, Pullen AE, Swager TM (2000) Chem Rev 100:2537–2574
2. Toal SJ, Trogler WC (2006) J Mater Chem 16:2871–2883
3. Singh S (2007) J Hazard Mater 144:15–28
4. Zhou Q, Swager TM (1995) J Am Chem Soc 117:12593–12602
5. Yang JS, Swager TM (1998) J Am Chem Soc 120:5321–5322
6. Amara JP, Swager TM (2005) Macromolecules 38:9091–9094
7. DiPasquale SJC, AG RAL, Trogler WC (2007) Chem Mater 19:6459–6470
8. Sanchez JC, Trogler WC (2008) J Mater Chem 18:3143–3156
9. Sanchez JC, Trogler WC (2008) Macromol Chem Phys 209:1527–1540
10. Sanchez JC, Urbas SA, Toal SJ, DiPasquale AG, Rheingold AL, Trogler WC (2008) Macromolecules 41:1237–1245
11. Sanchez JC, Toal SJ, Wang Z, Dugan RE, Trogler WC (2007) J Forensic Sci 52:1308–1313
12. Toal SJ, Sanchez JC, Dugan RE, Trogler WC (2007) J Forensic Sci 52:79–83
13. Toal SJ, Magde D, Trogler WC (2005) Chem Commun 43:5465–5467
14. Sohn H, Calhoun RM, Sailor MJ, Trogler WC (2005) Angew Chem 40:2104–2106

15. Sohn H, Sailor MJ, Magde D, Trogler WC (2003) J Am Chem Soc 125:3821–3830
16. Yamaguchi Y (1996) Synth Met 82:149–153
17. Yamaguchi S, Tamao K (1996) Bull Chem Soc Jpn 69:2327–2334
18. Toal SJ, Sohn H, Zakarov LN, Kassel WS, Golen JA, Rheingold AL, Trogler WC (2005) Organometallics 24:3081–3087
19. Kinnaird JWA, Ng PY, Kubota K, Wang X, Leighton JL (2002) J Am Chem Soc 124:7920–7921
20. Bouhadir G, Bourissou D (2004) Chem Soc Rev 33:210–217
21. Perozzi EF, Michalak RS, Figuly GD, Stevenson WH III, Dess DB, Ross MR, Martin JC (1981) J Org Chem 46:1049–1053
22. Sakurai H (1989) Synlett 1-8.
23. Fesik SW (1993) J Biomol NMR 3:261–269
24. Cheng J, Lepre CA, Moore JM (1994) Biochem 33:4093–4108
25. Shuker SB, Hajduk PJ, Meadows RP, Fesik SW (1996) Science 274:1531–1534
26. Schnur E, Turkov M, Kahn R, Gordon D, Gurevitz M, Anglister J (2008) Biochemistry 47:911–921
27. Kríz J, Dybal J, Makrlík E, Budka J (2008) Magn Reson Chem 46:235–243
28. Maria PC, Gal JF (1985) J Phys Chem 89:1296–1304
29. Saxena A, Fujiki M, Naito M, Okoshi K, Kwak G (2004) Macromolecules 37:5873–5879
30. Scatchard G (1949) Ann NY Acad Sci 51:660–672
31. Fielding L (2000) Tetrahedron 56:6151–6170
32. Ngowe CO, Bishop KD, McGuffin VL (2001) Anal Chim Acta 427:137–142
33. Cernia E, Delfini M, Di Cocco ME, Palocci C, Soro S (2002) Bioorg Chem 30:276–284
34. Delfini M, Bianchetti C, Di Cocco ME, Pescosolido N, Porcelle F, Rosa R, Rugo G (2003) Bioorg Chem 31:378–388
35. Bunte G, Hurttlen J, Pontius H, Hartlieb K, Krause H (2007) Anal Chim Acta 591:49–56