baua:
Bundesanstalt für Arbeitsschutz und Arbeitsmedizin
Federal Institute for Occupational Safety and Health

SUBSTANCE EVALUATION CONCLUSION

as required by REACH Article 48

and

EVALUATION REPORT

for

Bis(nonafluorobutyl)phosphinic acid (EC 700-183-3, CAS 52299-25-9)

Evaluating Member State(s): Germany

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Evaluating Member State Competent Authority

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Year of evaluation in CoRAP: 2018

The substance evaluation was concluded without requesting further information as the sole registrant ceased manufacture during the evaluation year.

Further information on registered substances here:

http://echa.europa.eu/web/guest/information-on-chemicals/registered-substances

DISCLAIMER

This document has been prepared by the evaluating Member State as a part of the substance evaluation process under the REACH Regulation (EC) No 1907/2006. The information and views set out in this document are those of the author and do not necessarily reflect the position or opinion of the European Chemicals Agency or other Member States. The Agency does not guarantee the accuracy of the information included in the document. Neither the Agency nor the evaluating Member State nor any person acting on either of their behalves may be held liable for the use which may be made of the information contained therein. Statements made or information contained in the document are without prejudice to any further regulatory work that the Agency or Member States may initiate at a later stage.

Foreword

Substance evaluation is an evaluation process under REACH Regulation (EC) No. 1907/2006. Under this process the Member States perform the evaluation and ECHA secretariat coordinates the work. The Community rolling action plan (CoRAP) of substances subject to evaluation, is updated and published annually on the ECHA web site[1].

Substance evaluation is a concern driven process, which aims to clarify whether a substance constitutes a risk to human health or the environment. Member States evaluate assigned substances in the CoRAP with the objective to clarify the potential concern and, if necessary, to request further information from the registrant(s) concerning the substance. If the evaluating Member State concludes that no further information needs to be requested, the substance evaluation is completed. If additional information is required, this is sought by the evaluating Member State. The evaluating Member State then draws conclusions on how to use the existing and obtained information for the safe use of the substance.

This Conclusion document, as required by Article 48 of the REACH Regulation, provides the final outcome of the Substance Evaluation carried out by the evaluating Member State. The document consists of two parts i.e. A) the conclusion and B) the evaluation report. In the conclusion part A, the evaluating Member State considers how the information on the substance can be used for the purposes of regulatory risk management such as identification of substances of very high concern (SVHC), restriction and/or classification and labelling. In the evaluation report part B the document provides explanation how the evaluating Member State assessed and drew the conclusions from the information available.

With this Conclusion document the substance evaluation process is finished and the Commission, the Registrant(s) of the substance and the Competent Authorities of the other Member States are informed of the considerations of the evaluating Member State. In case the evaluating Member State proposes further regulatory risk management measures, this document shall not be considered initiating those other measures or processes. Further analyses may need to be performed which may change the proposed regulatory measures in this document. Since this document only reflects the views of the evaluating Member State, it does not preclude other Member States or the European Commission from initiating regulatory risk management measures which they deem appropriate.

[1] http://echa.europa.eu/regulations/reach/evaluation/substance-evaluation/community-rolling-action-plan

Contents

Part A. Conclusion

1. CONCERN(S) SUBJECT TO EVALUATION

Bis(nonafluorobutyl)phosphinic acid (DPFBPA) was originally selected for substance evaluation in order to clarify concerns about:

- Suspected PBT/vPvB
- Exposure of environment
- High mobility in the environment

No further concerns were identified during the evaluation.

2. OVERVIEW OF OTHER PROCESSES / EU LEGISLATION

None.

3. CONCLUSION OF SUBSTANCE EVALUATION

The evaluation of the available information on the substance has led the evaluating Member State to the following conclusions, as summarised in the table below.

Table 1: Conclusion of Substance Evaluation

CONCLUSION OF SUBSTANCE EVALUATION Conclusions	Tick box
Need for follow-up regulatory action at EU level	
Harmonised Classification and Labelling	
Identification as SVHC (authorisation)	
Restrictions	
Other EU-wide measures	
No need for regulatory follow-up action at EU level	x

The sole registrant of DPFBPA ceased manufacture during the initial phase of the substance evaluation round. Therefore, no draft decision with further information requests to clarify the identified concerns was prepared by the eMSCA as there would be no addressee for these requests. Thus, the cease of manufacture did not occur as a reaction to a receipt of a draft decision according to article 50(3) as foreseen in the REACH regulation.
In the opinion of the eMSCA, the concerns for possible PBT/vPvB properties or other properties of concern of the substance remain open and should be reassessed in case the substance is re-registered in the future.

4. FOLLOW-UP AT EU LEVEL

4.1. Need for follow-up regulatory action at EU level

Not applicable.

4.1.1. Harmonised Classification and Labelling

Not applicable.

4.1.2. Identification as a substance of very high concern, SVHC (first step towards authorisation)

Not applicable.

4.1.3. Restriction

Not applicable.

4.1.4. Other EU-wide regulatory risk management measures

Not applicable.

5. CURRENTLY NO FOLLOW-UP FORESEEN AT EU LEVEL

5.1. No need for regulatory follow-up at EU level

Table 1: Reason for Removing Concern

REASON FOR REMOVED CONCERN The concern could be removed because	Tick box
Clarification of hazard properties/exposure	
Actions by the registrants to ensure safety, as reflected in the registration dossiers (Cease of manufacture)	x

The sole registrant of DPFBPA ceased manufacture during the evaluation phase. Therefore, there is no remaining use of the substance within the scope of substance evaluation. At the time this report was finalised, no other active registrations for DPFBPA were apparent.

The eMSCA recommends that further assessment of the as of yet unresolved hazard properties of the substance should be reinitiated in case the substance should be re-registered in the future.

5.2. Other actions

6. TENTATIVE PLAN FOR FOLLOW-UP ACTIONS (IF NECESSARY)

Not applicable.

Part B. Substance evaluation

7. EVALUATION REPORT

7.1. Overview of the substance evaluation performed

Bis(nonafluorobutyl)phosphinic acid was originally selected for substance evaluation in order to clarify concerns about:

- Suspected PBT/vPvB
- Exposure of environment
- High mobility in the environment

No further concerns were identified during the evaluation.

Table 2: Evaluated Endpoints

EVALUATED ENDPOINTS	
Endpoint evaluated	**Outcome/conclusion**
Persistence	*The evaluating MSCA concluded that further information will be potentially required to clarify the concern regarding persistence or possible degradation of the substance to short-chain perfluoroalkyl substances like perfluorbutanoic acid (PFBA). However, due to no active registrations for the substance at the end of the evaluation process, no further information on persistence was requested.*
Bioaccumulation	*The evaluating MSCA concluded that further information will be potentially required to clarify the concern regarding bioaccumulation. However, due to no active registrations for the substance at the end of the evaluation process, no further information on bioaccumulation was requested.*
Ecotoxicity	*The evaluating MSCA concluded that further information will be potentially required to clarify the concern regarding toxicity. However, due to no active registrations for the substance at the end of the evaluation*

	process, no further information on ecotoxicity was requested.
High mobility in the environment	*The evaluating MSCA concluded that further information will potentially be required to clarify the concern regarding mobility of possible degradation products (e.g. PFBA) in the environment. However, due to no active registrations for the substance at the end of the evaluation process, no further information on mobility was requested.*
Release into the environment	*The evaluating MSCA concluded that further information will potentially be required to clarify the concern regarding the release into the environment. However, due to no active registrations for the substance at the end of the evaluation process, no further information on environmental releases was requested.*

7.2. Procedure

Pursuant to Article 44(2) of the REACH Regulation, Bis(nonafluorobutyl)phosphinic acid was included on the Community rolling action plan (CoRAP) for evaluation in 2018. The Competent Authority of Germany was appointed to carry out the evaluation. The substance evaluation commenced on 26 March 2018.

The evaluation was targeted at environmental hazards and exposure.

As there were no further registrants of the substance at that time, the substance evaluation decision making process was concluded without a decision requesting further information.

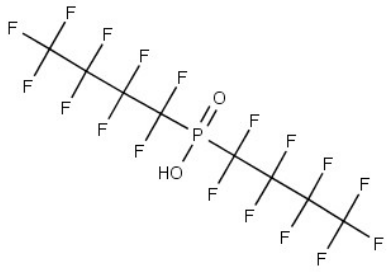
7.3. Identity of the substance

Table 3: Substance Identity

SUBSTANCE IDENTITY	
Public name:	bis(nonafluorobutyl)phosphinic acid
List number:	700-183-3
CAS number:	52299-25-9
Index number in Annex VI of the CLP Regulation:	-
Molecular formula:	$C_8HF_{18}O_2P$
Molecular weight range:	502 g/mol
Synonyms:	Phosphinic acid, bis(nonafluorobutyl)- P,P-Bis(1,1,2,2,3,3,4,4,4-nonafluorobutyl)phosphinic acid

Type of substance X Mono-constituent ☐ Multi-constituent ☐ UVCB

Structural formula:



7.4. Physico-chemical properties

Table 5: Overview of Physicochemical Properties

OVERVIEW OF PHYSICOCHEMICAL PROPERTIES	
Property	**Value**
Physical state at 20°C and 101.3 kPa	waxy, hygroscopic solid
Vapour pressure	0.00092 Pa at 20 °C 0.0023 Pa at 25 °C; 0.16 Pa at 50 °C; effusion method: vapour pressure balance
Water solubility	> 995 g/kg at 20 °C, pH < 20 °C flask method
Partition coefficient n-octanol/water (Log Kow)	Log Pow: 4, pH 1.2 (undissociated substance); shake flask method; Log Pow: 2.8 (sodium salt), calculation with Epiwin
Flammability	Not flammable
Explosive properties	-
Oxidising properties	-
Granulometry	-
Stability in organic solvents and identity of relevant degradation products	-
Dissociation constant	pKa 0.17 ±0.50; Most Acidic Temp: 25 °C; calculated

7.5. Manufacture and uses

7.5.1. Quantities

At the beginning of the substance evaluation process, the tonnage was reported to be in the range of 1-10 tonnes per annum in one active registration dossier. However, later during the substance evaluation phase the sole registrant ceased manufacture.

At the time of finalising this report, there were no active registrations for DPFBPA within the scope of substance evaluation.

Table 6: Aggregated Tonnages per Year

AGGREGATED TONNAGE (PER YEAR)				
☐ 1 – 10 t	☐ 10 – 100 t	☐ 100 – 1000 t	☐ 1000- 10,000 t	☐ 10,000-50,000 t
☐ 50,000 – 100,000 t	☐ 100,000 – 500,000 t	☐ 500,000 – 1000,000 t	☐ > 1000,000 t	☐ Confidential

7.5.2. Overview of uses

Table 7: Uses before cease of manufacture

USES	Use(s)
Uses as intermediate	Formulation of intermediates
Formulation	Formulation of intermediates, reactive and unreactive processing aids, metal surface treatment products and laboratory chemicals
Uses at industrial sites	Manufacture of the substance, formulation into mixtures, use as a laboratory reagent, use as an intermediate and as a reactive processing aid without inclusion into or onto articles and during roller application or brushing, use in chemical production or refinery in closed continuous or batch processes
Uses by professional workers	Formulation into mixtures, use as a laboratory reagent, use as an intermediate and as a reactive processing aid without inclusion into or onto articles and during roller application or brushing
Consumer Uses	None reported
Article service life	None reported

7.6. Classification and Labelling

7.6.1. Harmonised Classification (Annex VI of CLP)

No entry in Annex VI of CLP Regulation available.

7.6.2. Self-classification

- In the registration(s):

  - Acute Tox.3 (H301)
  - Eye Dam. 1 (H318)

- No additional hazard classes are notified among the aggregated self-classifications in the C&L Inventory.

7.7. Environmental fate properties

7.7.1. Degradation

7.7.1.1. Abiotic degradation

No relevant information in the registration dossier available.

Wang et al. assessed the publicly available information on the hazard properties of perfluoroalkyl phosphonic acids (PFPiAs) (Wang et al., 2016). The registered substance belongs to this substance group. PFPiAs are reactive under various conditions. Bis(nonafluorobutyl)phosphinic acid hydrolyses under heated (100°C) or alkalized (pH > 7 and < 12) conditions to yield perfluoroalkyl phosphonic acids (PFPAs) and $C_nF_{2n+1}H$. Under low NO_x conditions the latter one can react to form perfluorinated carboxylic acids (PFCAs) (Wang et al., 2014; Young et al., 2009; Young and Mabury, 2010). The chlorine atom initiated oxidation of C_4F_9H leads e.g. to small but detectable yields of trifluoroacetic acid (TFA), perfluoropropanoic acid (PFPrA) and perfluorbutanoic acid (PFBA) (Young et al., 2009).

In Patent EP2217652B1 the use of phosphinic acids in polymerisation processes are described. As part of the patent the hydrolysis of bis(nonafluorobutyl)phosphinic acid ($(C_4F_9)_2P(O)OH$) in alkaline solution was tested. Bis(nonafluorobutyl)phosphinic acid was mixed with 20% aqueous NaOH solution. Immediately a precipitation of $(C_4F_9)_2P(O)ONa$ was formed. Within three days and at room temperature, the precipitation dissolved completely due to hydrolysis of $(C_4F_9)_2P(O)ONa$ to $(C_4F_9)_2P(O)O(ONa)_2$. The formed product contains C_4F_9H which can be further transformed to PFCAs. The second step of hydrolysis to Na_3PO_4 takes place slowly.

7.7.1.2. Biodegradation

Biodegradation of bis(nonafluorobutyl)phosphinic acid was tested in one screening test. The substance is not readily biodegradable. No simulation test is available.

Table 8: Summary of screening tests on ready biodegradability

SUMMARY OF SCREENING TESTS		
Method	**Results**	**Reference**
OECD Guideline 301 F (Ready Biodegradability: Manometric Respirometry Test) adopted	% degradation of test substance: 0 after 28 days (O_2 consumption) Toxicity control: > 25% biodegradation in 14 days Reference substance: > 60% degradation by day 14	Registration dossier

7.7.1.3. Summary and discussion on degradation

Bis(nonafluorobutyl)phosphinic acid hydrolyses under heated or alkalized conditions. The transformation products can further be transformed to PFCAs (e.g. perfluorbutanoic acid – PFBA).

Bis(nonafluorobutyl)phosphinic acid is not readily biodegradable: 0% degradation was shown within 28 days.

7.7.2. Environmental distribution

Adsorption

No experimental data for adsorption to soil were available. Therefore, the log K_{oc} of 4.28 was estimated with EPISuite 4.11.

7.7.3. Bioaccumulation

The registrant provided test data and calculated data for log P_{ow}. The undissociated test substance has a log P_{ow} of 4 (pH 1.2) according to EU Method A.8. A log P_{ow} of 2.8 was calculated with Epiwin.

No experimental BCF-data are available.

Contrary to most other persistent organic pollutants, perfluoroalkyl substances have a low affinity to lipids but bind to proteins (Jones et al. 2003). Accurate data for protein binding of bis(nonafluorobutyl)phosphinic acid and its degradation products are not available.

Considering the substance's potential binding to proteins, the comparison of its calculated log K_{ow} against the cut-off value for the screening criterion for bioaccumulation (log K_{ow} of 4.5) is not straightforward as the latter is based on the bioaccumulation potential of lipophilic substances.

7.8. Environmental hazard assessment

The sole registrant of bis(nonafluorobutyl)phosphinic acid ceased manufacture during the initial phase of the evaluation round. The concerns for possible environmental hazard of the substance remain open and should be reassessed in case the substance is re-registered in the future.

Aquatic compartment (including sediment)

7.8.1.1. Fish

Not evaluated.

7.8.1.2. Aquatic invertebrates

Table 9:

SUMMARY OF EFFECTS ON AQUATIC INVERTEBRATES		
Method	**Results**	**Reference**
OECD Guideline 202 (Daphnia sp. Acute Immobilisation Test) Static *Daphnia magna*	EC_{50} (48 h) > 100 mg/L (nominal) based on: mobility	Registration dossier

7.8.1.3. Algae and aquatic plants

Table 10:

SUMMARY OF EFFECTS ON ALGAE AND AQUATIC PLANTS		
Method	**Results**	**Reference**
OECD Guideline 201 (Algae Growth Inhibition Test) static *Desmodesmus subspicatus*	EC_{50} (72 h) > 100 mg/L (nominal) based on: growth rate EC_{50} (72 h) > 100 mg/L (nominal) based on: biomass NOEC (72 h) ≥ 100 mg/L (nominal) based on: growth rate	Registration dossier

7.8.1.4. Sediment organisms

Not evaluated.

7.8.1.5. Other aquatic organisms

Not evaluated.

7.8.2. Terrestrial compartment

Not evaluated.

7.8.3. Microbiological activity in sewage treatment systems

Not evaluated.

7.8.4. PNEC derivation and other hazard conclusions

Not evaluated.

7.8.5. Conclusions for classification and labelling

As described above no exhaustive investigation was performed. Therefore no final conclusion for classification and labelling could be drawn.

7.9. Human Health hazard assessment

Not evaluated.

7.10. Assessment of endocrine disrupting (ED) properties

The sole registrant of bis(nonafluorobutyl)phosphinic acid ceased manufacture during the initial phase of the evaluation round. The concerns for possible endocrine disrupting properties of the substance remain open and should be reassessed in case the substance is re-registered in the future.

7.10.1. Endocrine disruption – Environment

According to chapter 7.7.1.3 PFBA is a possible transformation product.

Table 11: Effects of PFBA on the hypothalamus-pituitary-thyroid axis

PFBA	Domestic chicken/ herring gull, *in vitro* (embryonic neuronal cells)	Gene expression Domestic chicken: D2, D3, TTR, RC3, Oct1, MBP Herring gull: D2, RC3, Oct1	Domestic chicken: D2-, D3-, TTR-, RC3-, Oct1-, MBP- Herring gull: D2-, RC3-, Oct1-	Vongphachan, V., et al. (2011)
	Human, *in vitro*	Binding to TTR	-	Weiss, J. M., et al. (2009)
	Human, *in vitro*	Intrinsic/competitive binding to TR	-/-	Ren, X. M., et al. (2015)
	Rat, *in vitro*	HEX and PAX8 gene expression	+	Naile, J. E., et al. (2012)

7.10.2. Endocrine disruption - Human health

Not evaluated.

7.10.3. Conclusion on endocrine disrupting properties

As described above no exhaustive investigation was performed. Therefore no final conclusion regarding endocrine disrupting properties could be drawn.

7.11. PBT and VPVB assessment

The sole registrant of bis(nonafluorobutyl)phosphinic acid ceased manufacture during the initial phase of the evaluation round. The concerns for possible PBT/vPvB properties of the substance remain open and should be reassessed in case the substance is re-registered in the future.

7.12. Exposure assessment

7.12.1. Human health

Not evaluated.

7.12.2. Environment

For bis(nonafluorobutyl)phosphinic acid one registration existed in the tonnage band 1-10 tpa (ECHA dissemination side, 2018). The substance was used at industrial sites in formulations and by professional workers in mixtures for metal surface products and as intermediates. The following environmental release categories were summarised at the ECHA dissemination side:

ERC1: Manufacture of the substance

ERC2: Formulation into mixture

ERC4: Use of non-reactive processing aid at industrial site (no inclusion into or onto article)

ERC6a: Use of intermediate

ERC6b: Use of reactive processing aid at industrial site (no inclusion into or onto article)

Due to the above-mentioned shortcomings, it is not possible to conclude on possible risks for the environment from manufacture and uses of bis(nonafluorobutyl)phosphinic acid. Perfluorinated alcyl phosphinic acids are used as surrogate for already restricted PFCAs. Further, these substances are used as starting material for the preparation of various perfluoroalkyl-phosphorus compounds and they are of interest for the application in catalysis (Ignat'ev et al. 2015). Thus, in future an increasing use of these substances could be expected and may lead to a wide dispersive release to the environment.

However, during the substance evaluation decision making process the registration was revoked due to cease of manufacture. Therefore, no further exchange with the inactive registrant to clarify exposure of bis(nonafluorobutyl)phosphinic acid to the environment was initiated.

7.12.3. Combined exposure assessment

Not evaluated.

7.13. Risk characterisation

Not evaluated.

7.14. References

Ignat'ev, N. V., Bader, J., Koppe, K., Hoge, B., & Willner, H. (2015). Recent progress in perfluoroalkyl-phosphorus chemistry. *Journal of Fluorine Chemistry*, 171, 36-45.

Jones, P. D., Hu, W., De Coen, W., Newsted, J. L., & Giesy, J. P. (2003). Binding of perfluorinated fatty acids to serum proteins. *Environmental toxicology and chemistry*, *22*(11), 2639-2649.

Naile J.E., Wiseman S., Bachtold K., Jones P.D., and Giesy J.P. (2012): Transcriptional effects of perfluorinated compounds in rat hepatoma cells. *Chemosphere* 86 (3), 270-277. DOI: 10.1016/j.chemosphere.2011.09.044

Ren X.M., Zhang Y.F., Guo L.H., Qin Z.F., Lv Q.Y., and Zhang L.Y. (2015): Structure-activity relations in binding of perfluoroalkyl compounds to human thyroid hormone T3 receptor. *Arch. Toxicol.* 89 (2), 233-242. DOI: 10.1007/s00204-014-1258-y

Vongphachan V., Cassone C.G., Wu D., Chiu S., Crump D., and Kennedy S.W. (2011): Effects of perfluoroalkyl compounds on mRNA expression levels of thyroid hormone-responsive genes in primary cultures of avian neuronal cells. *Toxicol. Sci.* 120 (2), 392-402. DOI: 10.1093/toxsci/kfq395

Wang Z., Cousins I.T., Berger U., Hungerbühler K., and Scheringer M. (2016): Comparative assessment of the environmental hazards of and exposure to perfluoroalkyl phosphonic and phosphinic acids (PFPAs and PFPiAs): Current knowledge, gaps, challenges and research needs. *Environment International* 89–90, 235-247. DOI: 10.1016/j.envint.2016.01.023

Wang Z., Cousins I.T., Scheringer M., Buck R.C., and Hungerbühler K. (2014): Global Emission Inventories for C4-C14 Perfluoroalkyl Carboxylic Acid (PFCA) Homologues from 1951 to 2030, Part II: the Remaining Pieces of the Puzzle. *Environment International* 69, 166-176

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Young C.J., Hurley M.D., Wallington T.J., and Mabury S.A. (2009): Atmospheric chemistry of CF3CF2H and CF3CF2CF2CF2H: Kinetics and products of gas-phase reactions with Cl atoms and OH radicals, infrared spectra, and formation of perfluorocarboxylic acids. *Chemical Physics Letters* 473 (4), 251-256. DOI: 10.1016/j.cplett.2009.04.001

Young C.J. and Mabury S.A. (2010): Atmospheric perfluorinated acid precursors: chemistry, occurrence, and impacts. *Rev. Environ. Contam. Toxicol.* 208, 1-109. DOI: 10.1007/978-1-4419-6880-7_1

7.15. Abbreviations

CLP	Classification, Labelling and Packaging
CoRAP	Community rolling action plan
D	Deiodinase
DPFBPA	Bis(nonafluorobutyl)phosphinic acid
EC_{50}	Half maximal effect concentration
MBP	Myelin basic protein
Oct-1	Octamer motif-binding factor
OECD	Organisation for Economic Co-operation and Development
PFCAs	Perfluorinated carboxylic acids
PBT	Persistent, bioaccumulative and toxic
PFBA	Perfluorbutanoic acid
RC3	Neurogranin
TR	Thyroid receptor
TTR	Transtyretin
vPvB	Very persistent, very bioaccumulative