TC NES SUBGROUP ON IDENTIFICATION OF PBT AND VPVB SUBSTANCES

RESULTS OF THE EVALUATION OF THE PBT/VPVB PROPERTIES OF:

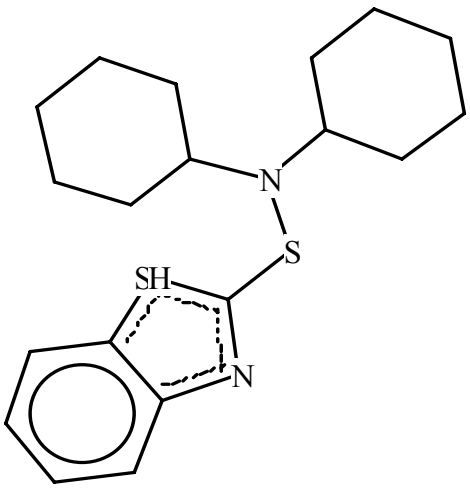
Substance name: N,N-dicyclohexylbenzothiazole-2-sulphenamide

EC number: 225-625-8

CAS number: 4979-32-2

Molecular formula: **C19H26N2S2**

Structural formula:



Summary of the evaluation:

N,N-dicyclohexylbenzothiazole-2-sulphenamide (DCBS) is not considered to be a PBT substance. It does not meet the P criterion due to a fast hydrolysis. Its hydrolysis products are expected to be mainly the same as its thermal decomposition products, dicyclohexylamine (CAS 101-83-7) and 2-mercaptobenzothiazole (CAS 149-30-4) followed by benzothiazole (CAS 95-16-9). Their persistence was not assessed for this report. DCBS fulfils the screening B criterion but it is not likely to be subject to relevant bioaccumulation in the environment due to the fast hydrolysis. The anticipated hydrolysis products do not fulfil the screening B criterion. For two of them, benzothiazole and mercaptobenzothiazole, experimental bioaccumulation data confirm that the B criterion is not met. Ecotoxicity of DCBS or its hydrolysis products was not assessed for this report.

JUSTIFICATION

1 IDENTIFICATION OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

Name: N,N-dicyclohexylbenzothiazole-2-sulphenamide
EC Number: 225-625-8
CAS Number: 4979-32-2
IUPAC Name:
Molecular Formula: C19H26N2S2
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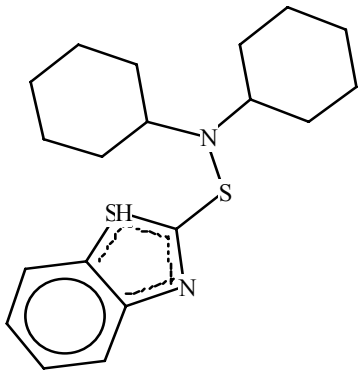

Molecular Weight: 346.55
Synonyms: 2-benzothiazolesulphenamide, N,N-dicyclohexyl; N,N,-dicyclohexyl-2-benzothiazolesulphenamide; DCBS (for full list of synonyms, see European Commission, 2000)

1.1 PURITY/IMPURITIES/ADDITIVES

No data available.

1.2 PHYSICO-CHEMICAL PROPERTIES

Table 1 Summary of physico-chemical properties. For references, see European Commission (2000) and OECD (2004)

REACH ref Annex, §	Property	Value	Comments
V, 5.1	Physical state at 20°C and 101.3 kPa	solid	European Commission (2000)
V, 5.2	Melting / freezing point	99°C	SRC online database (2004, as cited in OECD, 2004)
V, 5.3	Boiling point	> 200°C at 1013 hPa	Bayer AG data, as cited in European Commission (2000) (data not evaluated)
		> 300°C at 1013 hPa	MITI (1994b, as cited in OECD, 2004)
V, 5.5	Vapour pressure	< 7.0 · 10^{-5} Pa (at 100ºC)	MITI (1994b as cited in OECD, 2004)
V, 5.7	Water solubility	1.9 µg l^{-1} (at 25°C)	CERI (2001, as cited in OECD, 2004)
		30 mg l^{-1} (at 25 ºC)	Bayer AG data, as cited in European Commission (2000) (data not evaluated)
		0.054 mg l^{-1} (at 25 ºC)	WSKOW v1.41
V, 5.8	Partition coefficient n-octanol/ water (log value)	> 4.8	MITI (1994b, as cited in OECD, 2004)
		5.95	KOWWIN v1.67
VII, 5.19	Dissociation constant		

2 MANUFACTURE AND USES

Three companies have supplied information on the substance under Regulation 93/793/EEC. The substance is used solely as a curing agent (accelerator) in rubber industry (OECD, 2004; Bayer, 2003).

3 CLASSIFICATION AND LABELLING

The substance is not classified in the Annex I of Directive 67/548/EEC.

4 ENVIRONMENTAL FATE PROPERTIES

4.1 DEGRADATION (P)

4.1.1 Abiotic degradation

According to CERI (2001; as cited in OECD, 2004), N,N-dicyclohexylbenzothiazole-2-sulphenamide (DCBS) is hydrolysed rapidly. The hydrolysis half-life was determined to be 4.92 days at pH 4, 18.6 days at pH 7 and 112 days at pH 9 (all at 25°C). As the test concentration was above water solubility, the actual hydrolysis rate may be considerably faster. Dicyclohexylamine (CAS 101-83-7) and mercaptobenzothiazole (CAS 149-30-4) were anticipated by the authors to be the main degradation products based on mass spectrometry. Other degradation products were expected as well.

According to Bayer (1997), the substance has hydrolysis half-lives between 48 and 57 hours measured at pH 9, 7 and 4 and 25°C. Products expected to be formed are dicyclohexylamine and mercaptobenzothiazole, followed by benzothiazole (CAS 95-16-9) and some minor degradation products (Bayer, 2003). The substance is expected to react in the hydrolysis in a similar way as in the curing process, where thermal decomposition of the substance occurs. During vulcanization the unstable sulphur-nitrogen bond of benzothiazole sulphenamides is split with an intermediate formation of a 2-mercaptobenzothiazole (MBT) radical. Products resulting from the process are basic amines, benzothiazole derivatives, and further reaction products (GDCh, 1991). Further degradation products benzothiazole (BT; CAS 95-16-9), 2-methylbenzothiazole (MeBT; CAS 120-75-2), 2-methylthiobenzothiazole (CAS 615-22-5), benzothiazole sulphonic acid ($BTSO_3H$) and 2-hydroxybenzothiazole (BTon; CAS 934-34-9) are reported (e.g. Baumann and Ismeier, 1998; Reddy and Quinn, 1997; a review provided in European Commission, 2007).

Degradation data of the breakdown products were not reviewed for this report. They are reviewed in the EU risk assessment of N-cyclohexylbenzothiazole-2-sulphenamide (CAS 95-33-0; European Commission, 2007).

Indirect photochemical degradation in the atmosphere is considered to be fast for DCBS based on the estimated half-life of 3.4 hours for the reaction with OH-radicals using AOP v1.91 (24-hour day; $5 \cdot 10^5$ [OH] cm^{-3}).

4.1.2 Biotic degradation

Based on a ready biodegradability test (modified MITI-test) using predominantly domestic sludge, 2% of the substance was degraded in 28 days (Bayer AG data as cited in European Commission, 2000). It is noted that the study report was not available to the Rapporteur for evaluation. Due to the fast hydrolysis of the substance, the test has probably measured biodegradation of hydrolysis products.

Another screening biodegradability test was carried out according to OECD 301C (MITI 1994b as cited in OECD, 2004). The results showed 6% degradation in 28 days.

4.1.3 Other information [1]

Data not reviewed for this report.

4.1.4 Summary and discussion of persistence

DCBS undergoes a rapid hydrolysis according to two available hydrolysis studies. Hydrolysis products are expected to be the same breakdown products which are formed in the thermal decomposition. Primary hydrolysis products are expected to be dicyclohexylamine (CAS 101-83-7) and mercaptobenzothiazole (CAS 149-30-4), which further reacts to other benzothiazole derivatives. Same benzothiazole derivatives form in the hydrolysis and thermal decomposition of e.g. N-tert-butylbenzothiazole-2-sulphenamide (CAS 95-31-8; PBT summary no. 72) and N-cyclohexylbenzothiazole-2-sulphenamide (CAS 95-33-0). Data on the degradation of the environmentally most relevant hydrolysis/decomposition products are reviewed in the EU risk assessment of the last mentioned substance (European Commission, 2007).

[1] For example, half life from field studies or monitoring data

Based on two available ready biodegradability tests, the substance is considered as not readily biodegradable. However, it must be noted, that the tests may have measured biodegradation of the hydrolysis products of DCBS.

4.2 ENVIRONMENTAL DISTRIBUTION

Data not reviewed for this report.

4.2.1 Adsorption

4.2.2 Volatilisation

4.2.3 Long-range environmental transport

4.3 BIOACCUMULATION (B)

4.3.1 Screening data[2]

The reported logKow values of DCBS are between > 4.8 and 5.95. A BCF of 7,620 was calculated by BCFWIN v2.15 (logKow of 5.95 used). Estimated logKow values for the degradation products are:

Degradation product	**LogKow (KOWWIN v1.67)**
Dicyclohexylamine	4.37
Mercaptobenzothiazole	2.86
Benzothiazole	2.17
2-hydroxybenzothiazole	2.35
Methylbenzothiazole	2.72
Methylthiobenzothiazole	3.22
Benzothiazole sulphonic acid	-0.99 (based on smiles input; not included in the database)

Other logKow –values, which are in line with the above presented values are available e.g. in European Commission (2007).

4.3.2 Measured bioaccumulation data[3]

No experimental data are available for DCBS.

BCF has been measured for benzothiazole (MITI, 1992). Following the OECD 305C, bioconcentration factors for *Cyprinus carpio* were determined at 2.1 - 5.1 with a test concentration of 0.2 mg l^{-1} and at < 4.1 - 7.5 with a test concentration of 0.02 mg l^{-1}. Test duration was 6 weeks.

2 For example, log K_{ow} values, predicted BCFs

3 For example, fish bioconcentration factor

MITI (1992) has also tested mercaptobenzothiazole according to OECD 305C. A BCF of < 0.8 and a BCF < 8 were determined for *Cyprinus carpio* for exposure concentrations of 0.1 and 0.01 mg l^{-1}, respectively, during the test period of 6 weeks.

4.3.3 Other supporting information[4]

No data available.

4.3.4 Summary and discussion of bioaccumulation

No experimental data on bioaccumulation are available for DCBS. Despite the high logKow values (up to 5.95), it is considered that it is not necessary to assess further the bioaccumulation potential of DCBS. Due to the fast hydrolysis, exposure of the environment to the substance is unlikely or very low.

The hydrolysis products have calculated logKow values from –0.99 to 4.37. For benzothiazole and mercaptobenzothiazole experimental bioconcentration data have been derived according to OECD 305C. Experimental BCFs up to 7.5 were determined for benzothiazole and BCFs < 8 for mercaptobenzothiazole. Based on the estimated logKow –values and the two experimental BCF-values the breakdown products are considered having a low bioaccumulation potential.

5 HUMAN HEALTH HAZARD ASSESSMENT

Data not reviewed for this report.

6 ENVIRONMENTAL HAZARD ASSESSMENT

The available data on ecotoxicity were not reviewed for this report. A review of ecotoxicity data of the most relevant degradation products is provided in the EU risk assessment of N-cyclohexylbenzothiazole-2-sulphenamide (CAS 95-33-0; European Commission, 2007).

6.1 AQUATIC COMPARTMENT (INCLUDING SEDIMENT)

6.1.1 Toxicity test results

6.1.1.1 Fish

Acute toxicity

Long-term toxicity

[4]For example, measured concentrations in biota

6.1.1.2 Aquatic invertebrates

Acute toxicity

Long-term toxicity

6.1.1.3 Algae and aquatic plants

6.1.2 Sediment organisms

6.1.3 Other aquatic organisms

6.2 TERRESTRIAL COMPARTMENT

6.3 ATMOSPHERIC COMPARTMENT

7 PBT AND VPVB

7.1 PBT, VPVB ASSESSMENT

Persistence: N,N-dicyclohexylbenzothiazole-2-sulphenamide (DCBS) does not meet the P criterion due to a rapid hydrolysis. Hydrolysis half-lives between 48 and 57 hours at pH 4-9 have been determined. Hydrolysis products have not been identified in the available hydrolysis tests but they are expected to be the same as the thermal degradation products formed during its use in the vulcanization of rubber. Vulcanization breakdown products of DCBS are dicyclohexylamine, mercaptobenzothiazole, benzothiazole, 2-methylbenzothiazole, 2-hydroxybenzothiazole, 2-methylthiobenzothiazole and benzothiazole sulphonic acid. Degradation of these substances was not further reviewed for this report since they are not considered as PBT substances due to their low bioaccumulation potential.

Bioaccumulation: No experimental data on bioaccumulation of DCBS are available. DCBS meets the screening B criterion based on reported logKow values (up to 5.95). However, its bioaccumulation potential was not further assessed. Bioaccumulation of DCBS in the environment is expected to be very low or negligible due to the fast hydrolysis. Of the anticipated hydrolysis products experimental BCFs are available for benzothiazole (≤ 7.5) and mercaptobenzothiazole (< 8) and they are hence concluded to not fulfil the B criterion. The other degradation products do not meet the screening B criterion based on their estimated logKow –values.

Toxicity: Data on ecotoxicity were not reviewed for this report.

Summary: N,N-dicyclohexylbenzothiazole-2-sulphenamide (DCBS) does not meet the P criterion due to a fast hydrolysis. Main hydrolysis products are expected to be the same substances as formed during thermal decomposition of benzothiazole sulphenamides. Degradation of the expected hydrolysis products was not assessed for this report. DCBS meets the screening B criterion but it is not likely to be subject to relevant bioaccumulation due to the fast hydrolysis. Two anticipated hydrolysis products (benzothiazole and mercaptobenzothiazole) do not meet the B criterion. The

other degradation products do not fulfil the screening B criterion. Ecotoxicity data were not reviewed for this report. It is concluded that DCBS is not considered as a PBT substance.

INFORMATION ON USE AND EXPOSURE

Not relevant as the substance is not identified as a PBT.

OTHER INFORMATION

The information and references used in this report were taken from the following sources:

Baumann W and Ismeier M (1998) Kautschuk und Gummi. Daten und Fakten zum Umweltschutz. Springer Verlag Berlin Heidelberg.

Bayer (1997) Abiotic degradation of N,N-Diclyclohexylbenzothiazole-2-sulphenamid and N-tert-Butyl-2-benzothiazolesulphenamid as a function of pH according to the OECD test guideline 111. Antwerpen, 20.05.1997.

Bayer (2003) Personal communication. Email by Dr. Burkhardt Stock (Bayer) to German Federal Environment Agency on 24th April 2003.

European Commission (2007) European Risk Assessment Report, Draft of 04.07.2007, N-cyclohexylbenzothiazole-2-sulphenamide, CAS No: 95-33-0, EINECS No: 202-411-2.

European Commission (2000) IUCLID Dataset, N,N-dicyclohexyl-2-benzothiazolesulphenamide, CAS 4979-32-2, 18.2.2000.

GDCh (1991) 2-Mercaprobenzothiazole, BUA-Report 74; ed. by GDCh-Advisory Committee on Existing Chemicals of Environmental Relevance (BUA). S. Hirzel Verlag 1997.

MITI (1992) Biodegradation and Bioaccumulation data of Existing Chemicals based on CSCL Japan, Compiled under the Supervision of Chemical Products Safety Division, Basic Industries Bureau MITI, ed. by CITI, 1992. Published by Japan Chemical Industry Ecology-Toxicology & Information Center.

OECD (2004) SIDS Initial Assessment Report for SIAM 18, Paris, France, 20-23 April, 2004, N,N-dicyclohexyl-2-benzothiazolesulphenamide, CAS 4979-32-2. UNEP Publications.

Reddy M and Quinn JG (1997) Environmental Chemistry of Benzothiazoles derived from Rubber. Environ. Sci. Technol. 31(10), 2847-2853.