TC NES SUBGROUP ON IDENTIFICATION OF PBT AND VPVB SUBSTANCES

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

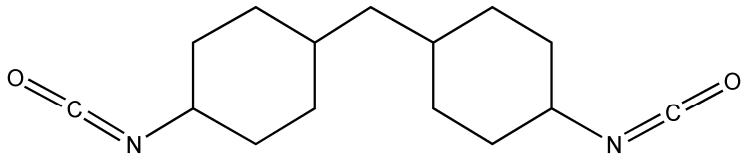
Substance name: 4,4'-methylenedicyclohexyl diisocyanate

EC number: 225-863-2

CAS number: 5124-30-1

Molecular formula: C15H22N2O2

Structural formula:



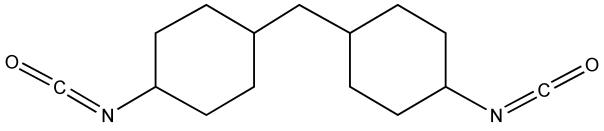
Summary of the evaluation:

4,4'-methylenedicyclohexyl diisocyanate is not considered to be a PBT substance. The substance does not meet the P criterion for aquatic environment due to a fast hydrolysis. The screening B criterion is fulfilled but the bioaccumulation potential was not further assessed due to the fast hydrolysis. The hydrolysis product expected to be formed under environmental conditions is 4,4'-diaminodicyclohexylmethane (CAS 1761-71-3). This substance fulfils the P/vP criteria according to screening data, but it does not fulfil the screening B criterion. The assessment of ecotoxicity was not completed.

JUSTIFICATION

1 IDENTIFICATION OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

Name: 4,4’-methylenedicyclohexyl diisocyanate
EC Number: 225-863-2
CAS Number: 5124-30-1
IUPAC Name:
Molecular Formula: C15H22N2O2
Structural Formula:



Molecular Weight: 262.35
Synonyms: Dicyclohexylmethane-4,4’-diisocyanate; methylenebis-(4-cyclohexylisocynate): for full list of synonyms, see OECD (2005)

1.1 PURITY/IMPURITIES/ADDITIVES

A typical composition of 4,4’-methylenedicyclohexyl diisocyanate was specified by Dieterich and Uhlig (2002 as cited in OECD, 2005) with a purity of 92% 4,4’-methylene-dicyclohexyl diisocyanate and the corresponding isomeric composition:

- *cis,cis*-isomer 14%
- *cis,trans*-isomer 58%
- *trans,trans*-isomer 20%
- others 8% (2,4'-methylenedicyclohexyl diisocyanate).

The commercial product of 4,4’-methylenedicyclohexyl diisocyanate also contains 2,4’-methylenedicyclohexyl diisocyanate (Bayer MaterialScience AG, 2004a as cited in OECD, 2005).

1.2 PHYSICO-CHEMICAL PROPERTIES

Table 1 Summary of physico-chemical properties. For details and references, see OECD (2005). Data cited in Table 1 have not been re-evaluated separately for the PBT assessment

REACH ref Annex, §	Property	Value	Comments
V, 5.1	Physical state at 20 C and 101.3 Kpa	liquid	
V, 5.2	Melting / freezing point	15°C	Dieterich and Uhlig (2002)
V, 5.3	Boiling point	167-168°C (at 2 hPa)	GIAP (1969)
V, 5.5	Vapour pressure	$2.13 \cdot 10^{-5}$ hPa at 25 °C	Bayer AG (1994a)
V, 5.7	Water solubility	Not determinable due to hydrolysis 0.121 mg l^{-1} at 25°C	Bayer AG Calculated (WSKOW v1.41)
V, 5.8	Partition coefficient n-octanol/water (log value)	Not determinable due to hydrolysis 6.11	Bayer AG Calculated (KOWWIN v1.67)
VII, 5.19	Dissociation constant	-	

2 MANUFACTURE AND USES

Two companies have provided information on the substance under Regulation 93/793/EEC. The global production capacity of 4,4'-methylenedicyclohexyl diisocyanate is 10,000 - 20,000 tonnes/annum (Bayer Material Science AG, 2004a as cited in OECD, 2005).

3 CLASSIFICATION AND LABELLING

The substance is classified in the Annex I of Directive 67/548/EEC:

Xn; R23 Toxic by inhalation

Xi; R36/37/38 Irritating to eyes, respiratory system and skin

Xi; R42/43 May cause sensitization by inhalation and skin contact

4 ENVIRONMENTAL FATE PROPERTIES

4.1 DEGRADATION (P)

4.1.1 Abiotic degradation

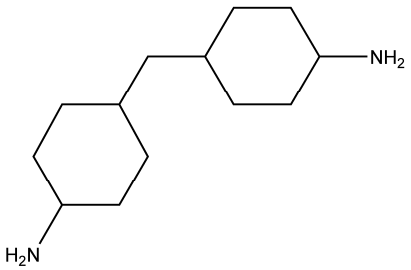
Indirect photochemical degradation in the atmosphere is considered to be fast based on the estimated half-life of 15 hours for the reaction with OH-radicals using AOP v1.91 (24 h day^{-1}; $5 \cdot 10^5$ OH^- cm^{-3}).

Hydrolysis of 4,4'-methylenedicyclohexyl diisocyanate was screened in a non-standard manner dissolving 10 ml of test substance to 40 ml acetonitrile and filling the flask to 100 ml with water (Bayer AG, 1999). The decrease of test substance concentration was monitored by measuring every 20 minutes the NCO-content with GC/FID analysis. The test substance was observed to be stable in pure acetonitrile. Hydrolysis half-life was determined to be 2 hours in the test. Incubation temperature was approximately 23.5°C but it is noted, that the pH of the test solution was not followed. Therefore the rate of hydrolysis observed in the test can only be considered indicative for environmentally relevant conditions.

A preliminary test according to OECD 111 was carried out with 4,4'-methylenedicyclohexyl diisocyanate to determine the degradation products in water (Bayer Industry Services, 2004). A solution of 2.64 g l^{-1} was incubated in demineralised, unbuffered water at 50°C during 5 days under continuous stirring. pH of the test solution was not monitored during the test.

In the aqueous phase the three isomers of 4,4'-methylenebis(cyclohexylamine) (CAS 1761-71-3) were identified with GC- and HPLC-MS. Additionally, the HPLC-analysis showed to a minor extent traces of a trimeric diamine compound; this was bound by urea-groups. During the test, insoluble droplets formed and adhered to the glass walls. They were analysed with IR spectroscopy and were found to contain urea components (polymeric urea) and encapsulated traces of isocyanate-groups (Bayer Industry Services, 2004). This hydrolysis product is inert and due to its large size not bioavailable. In addition, this substance can be assumed to be formed only in very high isocyanate concentrations, and hence is not relevant for the environment.

Reading across from hydrolysis data on a structurally similar substance hexamethylene diisocyanate (CAS 822-06-6; OECD, 2001) and considering the two screening type of hydrolysis tests described above, it can be assumed that the isocyanate groups of 4,4'-methylenedicyclohexyl diisocyanate react with water forming the corresponding diamine (4,4'-diaminodicyclohexylmethane; CAS 1761-71-3; see structure below) and CO_2.



4,4'-diaminodicyclohexylmethane (CAS 1761-71-3)

Furthermore, reading across from data on hexamethylene diisocyanate (OECD, 2001) and considering the results of Bayer Industry Services (2004), 4,4'-methylenedicyclohexyl diisocyanate can also react with already formed corresponding amine or diamine and form this way oligourea or polyurea. However, this reaction is not expected to occur in environmentally relevant concentrations and the resulting molecules would be due to their size not bioavailable.

4.1.2 Biotic degradation

4,4'-methylenedicyclohexyl diisocyanate was tested according to the manometric respirometry test method of 79/831/EEC, Annex V Part C (Bayer AG data, as cited in European Commission, 2000a). Test concentration was 12 mg l^{-1} and test substance purity 91.6% (no data on impurities). 0% degradation was observed by the day 28. It must be noted that the method measures biodegradation by means of oxygen demand and hence it can be concluded that the parent

compound and the hydrolysis product 4,4'-diaminodicyclohexylmethane formed did not biodegrade within the 28-day test. The test report was not available to the Rapporteur for evaluation.

BIOWIN v4.02 predicts that the substance is not readily biodegradable, but on the other hand, BIOWIN 3 (= 2.6) predicts that the substance is not persistent.

For the expected hydrolysis product 4,4'-diaminodicyclohexylmethane, BASF AG (1986 as cited in European Commission, 2000b) has reported that a standard Zahn-Wellens test resulted 20% degradation. No further details on test conditions are available. The result would indicate that the substance is not inherently biodegradable. It must be noted that the test report was not available to the Rapporteur for evaluation. BIOWIN v4.02 predicts overall no ready biodegradability but BIOWIN 3 (= 2.8) predicts that the substance is not persistent.

An aromatic diamine similar to the hydrolysis product is 4,4'-methylenedianiline (4,4'MDA; CAS 101-77-9), which has been subject to EU risk assessment. The risk assessment concludes that the substance is not readily biodegradable and that it is inherently biodegradable only using adapted inoculum (European Commission, 2001).

4.1.3 Other information [1]

4.1.4 Summary and discussion of persistence

Reading across from data on structurally similar substance hexamethylene diisocyanate (CAS 822-06-6; OECD, 2001) and considering the two screening type of hydrolysis tests with 4,4'-methylenedicyclohexyl diisocyanate (Bayer AG, 2004; Bayer Industry Services, 2004), the substance is expected to be hydrolysed rapidly forming 4,4'-diaminodicyclohexylmethane (CAS 1761-71-3) and carbon dioxide in environmentally relevant exposure concentrations. Hence, the parent substance itself is not considered persistent in the aquatic environment.

The available ready biodegradability test on 4,4'-methylenedicyclohexyl diisocyanate measured biodegradation of both the parent substance and its hydrolysis product and resulted 0% biodegradation. In addition, a Zahn-Wellens test (BASF AG, 1986) for the hydrolysis product 4,4'-diaminodicyclohexylmethane indicates that it is not inherently biodegradable. The assessment of its aromatic form 4,4'-MDA, which is not inherently biodegradable in non-adapted conditions (European Commission, 2001), also supports the conclusion.

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

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

4.3 BIOACCUMULATION (B)

4.3.1 Screening data[2]

A predicted BCF of 10,190 was obtained using BCFWIN v2.15 and the estimated log Kow of 6.11.

The expected hydrolysis product 4,4'-diaminodicyclohexylmethane has a logKow of 3.26 based on the estimation of KOWWIN v1.67. A logKow of 2.03 measured according to OECD 107 (shake-flask method) has been reported by BASF AG (1988, as cited in European Commission, 2000b). The test report was not available for the Rapporteur for evaluation. Using the highest logKow -value, a BCF of 65 has been estimated by BCFWIN v2.15.

4.3.2 Measured bioaccumulation data[3]

No data available.

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 4,4'-methylenedicyclohexyl diisocyanate. Although 4,4'-methylenedicyclohexyl diisocyanate has a high estimated logKow (6.11), it is considered that it is not necessary to assess further the bioaccumulation potential. Due to the fast hydrolysis, exposure of the environment to the substance is unlikely or very low. The expected hydrolysis product 4,4'-diaminodicyclohexylmethane has based on its estimated and measured octanol-water partitioning coefficients (logKow 3.26 and 2.03, respectively) and predicted BCF (65) a low or moderate bioaccumulation potential.

5 HUMAN HEALTH HAZARD ASSESSMENT

Data not reviewed for this report.

6 ENVIRONMENTAL HAZARD ASSESSMENT

6.1 AQUATIC COMPARTMENT (INCLUDING SEDIMENT)

Due to the fast hydrolysis, 4,4'-methylenedicyclohexyl diisocyanate should be tested in flow-through conditions. The available data on fish toxicity presented in the IUCLID (European Commission 2000a) originate from static tests and are hence expected to reflect mainly the ecotoxicity of the hydrolysis product 4,4'-diaminodicyclohexylmethane. The test data available in the European Commission (2000b) on the ecotoxicity of the hydrolysis product indicate

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

3 For example, fish bioconcentration factor

4For example, measured concentrations in biota

LC_{50}-values > 0.1 mg l^{-1} to fish. It must be noted, that the ecotoxicity data were not evaluated because the test reports were not available to the Rapporteur.

6.1.1 Toxicity test results

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: 4,4'-methylenedicyclohexyl diisocyanate does not meet the P criterion for aquatic environment due to a fast hydrolysis. Based on data of structurally similar hexamethylene diisocyanate (CAS 822-06-6) and considering the available hydrolysis test results for 4,4'-methylenedicyclohexyl diisocyanate, the expected hydrolysis product under environmental conditions is 4,4'-diaminodicyclohexylmethane (CAS 1761-71-3). This substance is, based on limited data, not inherently biodegradable and it is therefore considered fulfilling the screening P/vP criteria.

Bioaccumulation: The substance fulfils due to the high logKow (6.11) the screening B criterion but no further testing is necessary due to the overall conclusion (see below) and due to the fast hydrolysis of the substance. For the environmentally relevant hydrolysis product 4,4'-diaminodicyclohexylmethane logKow –values of 2.03 and 3.26 are available. It is concluded, that the hydrolysis product does not fulfil the screening B criterion.

Toxicity: The assessment of ecotoxicity was not completed.

Summary: 4,4'-methylenedicyclohexyl diisocyanate does not meet the P criterion for aquatic environment due to a fast primary degradation via hydrolysis. The screening B criterion is fulfilled, but no further information is needed on bioaccumulation due to the fast hydrolysis. The hydrolysis product expected to be formed under environmental conditions is 4,4'-diaminodicyclohexylmethane (CAS 1761-71-3). This substance fulfils the P/vP criteria based on screening data, but it does not fulfil the screening B criterion. The assessment of ecotoxicity was not completed. It is concluded that 4,4'-methylenedicyclohexyl diisocyanate 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:

Bayer Industry Services GmbH & Co. OHG (2004) Hydrolysis as a Function of pH and Temperature of Desmodur W, Rresults of Preliminary Test. Study No. A 04/0044/01 LEV.

Bayer AG (1999) Decrease of NCO-Content in Water. Final Report. File Number 99/0049/01/LEV, May 14, 1999.

European Commission (2001) European Union Risk Assessment Report, 4,4'-Methylenedianiline, CAS No: 101-77-9, EINECS No: 202-974-4, 1st Priority list, Vol. 9. EUR 19727 EN.

European Commission (2000) IUCLID Dataset, 4,4'-methylenedicyclohexyl diisocyanate, CAS 5124-30-1, 18.2.2000.

European Commission (2000b) IUCLID Dataset, 4,4'-diaminodicyclohexylmethane, CAS 1761-71-3, 18.2.2000.

OECD (2005) Draft SIDS Initial Assessment Report for SIAM 20, Paris France, 19-22 April 2005. 4,4'-methylenedicyclohexyl diisocyanate, CAS No. 5124-30-1.

OECD (2002) SIDS Initial Assessment Report for SIAM 12, Paris, France, March, 2001. 1,6-hexamethylene diisocyanate/HDI, CAS No. 822-06-0. UNEP Publications.