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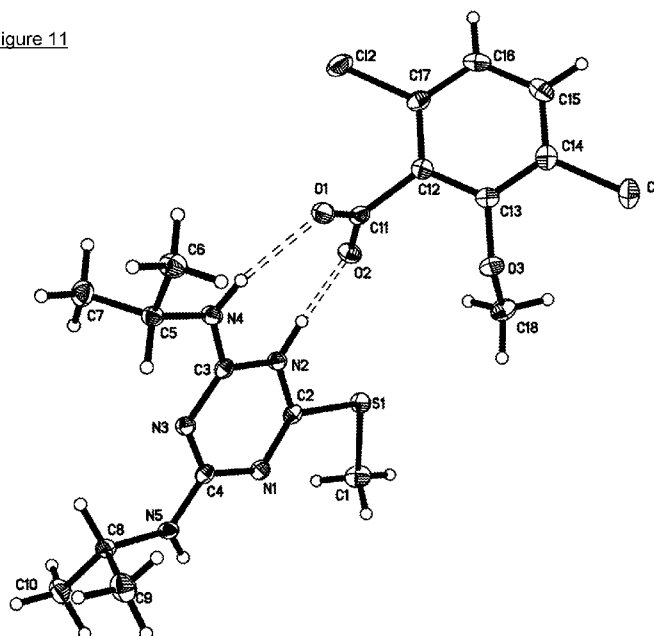
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(54) Title: MOLECULAR COMPLEXES COMPRISING DICAMBA AND A TRIAZINE HERBICIDE

Figure 11



(57) Abstract: Molecular complexes comprising 3,6-dichloro-2-methoxybenzoic acid (dicamba) and a compound selected from the group of triazine herbicides are described, together with compositions comprising such molecular complexes, and methods of their preparation.



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MOLECULAR COMPLEXES COMPRISING DICAMBA AND A TRIAZINE HERBICIDE**FIELD OF THE INVENTION**

This invention relates to molecular complexes of herbicide compounds. In particular this invention relates to molecular complexes comprising 3,6-dichloro-2-methoxybenzoic acid
5 and a triazine herbicide, and to herbicidal compositions comprising such molecular complexes.

BACKGROUND OF THE INVENTION

3,6-dichloro-2-methoxybenzoic acid (dicamba) is a selective systemic herbicide which is used to control annual and perennial grasses and broad-leaf weeds.

10 An increasing number of weed populations have been identified which show resistance to dicamba, and the spread of these resistant populations could have a significant impact on the effectiveness of this herbicide. One strategy to overcome such issues is the use of dicamba in combination with one or more additional herbicide compounds with
15 alternative modes of action. The development of a single formulation containing each of the herbicide compounds to be applied in combination is attractive. For example, the development of such formulations can reduce the need for multiple applications of herbicide, can help to ensure consistent delivery of the desired ratio of each herbicide compound, and can reduce delivery costs.

However, the development of such formulations incorporating dicamba is challenging.
20 For example, a single combination formulation must provide conditions in which both dicamba and additional herbicide compounds are stable. In addition, the relatively high aqueous solubility of dicamba may make consistent application with less soluble compounds problematic. Furthermore, formulations comprising dicamba may suffer from loss from the site of application due to the relatively high volatility and aqueous solubility
25 of dicamba.

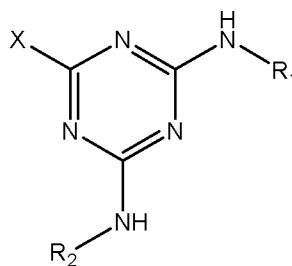
There remains a need to develop new stable herbicide formulations containing dicamba which overcome one or more of the issues identified above.

SUMMARY OF THE INVENTION

The present inventors have surprisingly found that triazine herbicides may be used to
30 form molecular complexes with 3,6-dichloro-2-methoxybenzoic acid (dicamba). The molecular complexes have been found to have high stability and provide dicamba in a form which has reduced aqueous solubility and lower volatility.

Therefore, in a first aspect of the invention there are provided molecular complexes of 3,6-dichloro-2-methoxybenzoic acid (dicamba) and a compound selected from the group of triazine herbicides.

Triazine herbicides of particular utility may be represented by formula (I):



(I)

wherein X = Cl, -OCH₃, or -SCH₃; R₁ = ethyl or isopropyl; R₂ = ethyl, iso-propyl, cyclopropyl, tert-butyl, or -C(CH₃)₂CN.

Preferably, the triazine herbicide is selected from atrazine, simazine, cyanazine, propazine, terbutryn, prometryn or ametryn. More preferably, the triazine herbicide is selected from atrazine, cyanazine, terbutryn, prometryn or ametryn. Typically, the molar ratio of dicamba: triazine herbicide 1:1.

Typically, the molecular complexes may be formed by solution or slurry crystallisation processes. Therefore, in a second aspect of the invention there is provided a method for the preparation of molecular complexes as described herein which comprises combining dicamba and a triazine herbicide in a suitable solvent.

In a third aspect of the invention there is provided a herbicidal composition comprising particles of a molecular complex as described herein and at least one agriculturally acceptable carrier. Typically, such compositions may be in the form of a solid formulation, such as a powder or granulated composition, or may be a liquid formulation, such as an aqueous suspension concentrate or a suspo-emulsion.

In a fourth aspect of the invention, there is provided the use such herbicidal compositions for controlling undesired vegetation, for example during crop cultivation.

In a fifth aspect of the invention there is provided a method for controlling undesired vegetation comprising contacting the vegetation with a composition comprising particles of a molecular complex as described herein and at least one agriculturally acceptable carrier.

DEFINITIONS

The term “about” or “approximately” means an acceptable error for a particular value as determined by a person of ordinary skill in the art, which depends in part on how the value is measured or determined. In certain embodiments, the term “about” or

5 “approximately” means within 1, 2, 3 or 4 standard deviations. In certain embodiments, the term “about” or “approximately” means within 30%, 25%, 20%, 15%, 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, 1%, or 0.5% of a given value or range. In certain embodiments and with reference to X-ray powder diffraction two-theta peaks, the terms “about” or “approximately” means within $\pm 0.2^\circ 2\theta$.

10 The term “ambient temperature” means one or more room temperatures between about 15 °C to about 30 °C, such as about 15 °C to about 25 °C.

The term “crystalline” and related terms used herein, when used to describe a compound, substance, modification, material, component or product, unless otherwise specified, means that the compound, substance, modification, material, component or

15 product is substantially crystalline as determined by X-ray diffraction. See, e.g., Remington: The Science and Practice of Pharmacy, 21st edition, Lippincott, Williams and Wilkins, Baltimore, Md. (2005); The United States Pharmacopeia, 23rd ed., 1843-1844 (1995).

The term “overnight” refers to the period of time between the end of one working day to

20 the subsequent working day in which a time frame of about 12 to about 18 hours has elapsed between the end of one procedural step and the instigation of the following step in a procedure.

“Slurry” means a heterogeneous mixture of at least a portion of the molecular complex in one or more solvents. “Slurry” therefore includes a mixture of molecular complex which

25 is partially present as a solid, as well as being partially dissolved in the one or more solvents.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows a representative x-ray powder diffraction pattern of the molecular complex of Example 1.

30 Figure 2 shows a representative differential scanning calorimetry (DSC) curve of the molecular complex of Example 1.

Figure 3 shows a representative x-ray powder diffraction pattern of the molecular complex of Example 2.

Figure 4 shows a representative differential scanning calorimetry (DSC) curve of the molecular complex of Example 2.

- 5 Figure 5 shows a representative x-ray powder diffraction pattern of the molecular complex of Example 3.

Figure 6 shows a representative differential scanning calorimetry (DSC) curve of the molecular complex of Example 3.

- 10 Figure 7 shows a representative x-ray powder diffraction pattern of the molecular complex of Example 4.

Figure 8 shows a representative differential scanning calorimetry (DSC) curve of the molecular complex of Example 4.

Figure 9 shows a representative x-ray powder diffraction pattern of the molecular complex of Example 5.

- 15 Figure 10 shows a representative differential scanning calorimetry (DSC) curve of the molecular complex of Example 5.

Figure 11 shows a view of a prometryn: dicamba unit from the crystal structure of Example 4.

DETAILED DESCRIPTION OF THE INVENTION

- 20 Preferred and/or optional features of the invention will now be set out. Any aspect of the invention may be combined with any other aspect of the invention unless the context demands otherwise. Any of the preferred and/or optional features of any aspect may be combined, either singly or in combination, with any aspect of the invention unless the context demands otherwise.

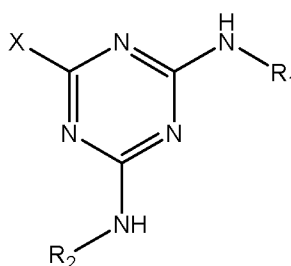
- 25 The present invention relates to an isolated molecular complex comprising 3,6-dichloro-2-methoxybenzoic acid (dicamba) and a compound selected from the group of triazine herbicides, and to herbicidal compositions comprising such crystalline materials.

- A molecular complex is a crystalline material composed of two or more different components which has a defined single-phase crystal structure. The components are
30 held together by non-covalent bonding, such as hydrogen bonding, ionic bonding, van der Waals interactions, π - π interactions, etc. The term molecular complex includes

salts, co-crystals and salt/co-crystal hybrids. In one embodiment, the molecular complex is a salt. In another embodiment, the molecular complex is a co-crystal. In another embodiment, the molecular complex is a salt/co-crystal hybrid.

- Without wishing to be bound by theory, it is believed that when the molecular complex is a co-crystal, the co-crystal demonstrates improved physiochemical properties, such as crystallinity, solubility properties and/or modified melting points. In certain embodiments, the melting point of the molecular complex may be higher than the melting point of dicamba itself and/or the triazine itself. In this instance, a higher melting point may be of benefit in the preparation of, for example, a suspension concentrate formulation of the molecular complex. In certain embodiments, the melting point of the molecular complex may be lower than the melting point of dicamba itself and/or the triazine itself. In this instance, a lower melting point may be of benefit in the preparation of, for example, an encapsulated formulation of the molecular complex or liquid formulation of the molecular complex.
- The molecular complexes may be distinguished from mixtures of dicamba and the selected triazine herbicide by standard analytical means which are well known to those skilled in the art, for example x-ray powder diffraction (XRPD), single crystal x-ray diffraction, or differential scanning calorimetry (DSC). The molar ratio of the components of the molecular complex may be determined using, for example, HPLC or ^1H NMR.
- The molecular complexes comprise 3,6-dichloro-2-methoxybenzoic acid (dicamba) and a triazine herbicide. Triazine herbicides are well known to those skilled in the art and comprise a tri-substituted 1,3,5-triazine core.

Triazine herbicides of particular utility may be represented by formula (I):



25

(I)

wherein X = Cl, -OCH₃, or -SCH₃; R₁ = ethyl or isopropyl; R₂ = ethyl, iso-propyl, cyclopropyl, tert-butyl, or -C(CH₃)₂CN.

Preferably, X = Cl or -SCH₃, more preferably X = Cl.

Further preferred compounds have X = -OCH₃, R₁ = isopropyl, and R₂ = isopropyl; or X = -SCH₃, R₁ = ethyl or iso-propyl, and R₂ = iso-propyl or tert-butyl.

Preferably, the triazine herbicide is selected from atrazine (6-chloro-4-N-ethyl-2-N-(propan-2-yl)-1,3,5-triazine-2,4-diamine), simazine (6-chloro-2-N,4-N-diethyl-1,3,5-triazine-2,4-diamine), cyanazine (2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropanenitrile), propazine (6-chloro-2-N,4-N-di(propan-2-yl)-1,3,5-triazine-2,4-diamine), terbutryn (2-N-tert-butyl-4-N-ethyl-6-methylsulfanyl-1,3,5-triazine-2,4-diamine), prometryn (6-methylsulfanyl-2-N,4-N-di(propan-2-yl)-1,3,5-triazine-2,4-diamine) or ametryn (4-N-ethyl-6-methylsulfanyl-2-N-propan-2-yl-1,3,5-triazine-2,4-diamine). More preferably, the triazine herbicide is selected from atrazine (6-chloro-4-N-ethyl-2-N-(propan-2-yl)-1,3,5-triazine-2,4-diamine), cyanazine (2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropanenitrile), propazine (6-chloro-2-N,4-N-di(propan-2-yl)-1,3,5-triazine-2,4-diamine), terbutryn (2-N-tert-butyl-4-N-ethyl-6-methylsulfanyl-1,3,5-triazine-2,4-diamine), prometryn (6-methylsulfanyl-2-N,4-N-di(propan-2-yl)-1,3,5-triazine-2,4-diamine) or ametryn (4-N-ethyl-6-methylsulfanyl-2-N-propan-2-yl-1,3,5-triazine-2,4-diamine)

In one embodiment, the present invention relates a molecular complex comprising, or consisting essentially of, dicamba and terbutryn (2-N-tert-butyl-4-N-ethyl-6-methylsulfanyl-1,3,5-triazine-2,4-diamine). The molar ratio of dicamba: terbutryn is generally in the range from 1:1 to 2:1, such as 1:1. However, variations are possible which typically do not exceed 20 mol% and preferably do not exceed 10 mol%.

In the case that the molar ratio of dicamba: terbutryn is 1:1, the current inventors have identified a crystalline form which exhibits an x-ray powder diffraction pattern (Cu K α radiation) substantially as shown in Figure 1. The XRPD degree 2-theta ($^{\circ}$ 2 θ) values are shown in Table 1. Preferably, the molecular complex shows at least 5, preferably at least 8 or at least 12, more preferably at least 15, even more preferably at least 20, or all of the reflexes shown in Table 1 as degree 2-Theta ($^{\circ}$ 2 θ) values $\pm$ 0.2 degrees 2-theta. The crystalline form may also be identified by its differential scanning calorimetry (DSC) curve as shown in Figure 2, in particular by the melting point temperature with an onset temperature of about 124.3 $^{\circ}$ C as determined by DSC.

In another embodiment, the present invention relates to a molecular complex comprising, or consisting of, dicamba and atrazine (6-chloro-4-N-ethyl-2-N-(propan-2-yl)-1,3,5-triazine-2,4-diamine). The molar ratio of dicamba: atrazine is generally in the range from

1:1 to 2:1, such as 1:1. However, variations are possible which typically do not exceed 20 mol% and preferably do not exceed 10 mol%.

In the case that the molar ratio of dicamba: atrazine is 1:1, the current inventors have identified a crystalline form which exhibits an x-ray powder diffraction pattern (Cu K α radiation) substantially as shown in Figure 3. The XRPD degree 2-theta ($^{\circ}$ 2 θ) values are shown in Table 2. Preferably, the molecular complex shows at least 5, preferably at least 8 or at least 12, more preferably at least 15, even more preferably at least 20, or all of the reflexes shown in Table 2 as degree 2-Theta ($^{\circ}$ 2 θ) values $\pm$ 0.2 degrees 2-theta. The crystalline form may also be identified by its differential scanning calorimetry (DSC) curve as shown in Figure 4, in particular by the melting point temperature with an onset temperature of about 81.6 $^{\circ}$ C as determined by DSC.

In a further embodiment, the present invention relates to a molecular complex comprising, or consisting of, dicamba and cyanazine ((2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropanenitrile). The molar ratio of dicamba: cyanazine is generally in the range from 1:1 to 2:1, such as 1:1. However, variations are possible which typically do not exceed 20 mol% and preferably do not exceed 10 mol%.

In the case that the molar ratio of dicamba and cyanazine is 1:1, the current inventors have identified a crystalline form which exhibits an x-ray powder diffraction pattern (Cu K α radiation) substantially as shown in Figure 5. The XRPD degree 2-theta ($^{\circ}$ 2 θ) values are shown in Table 3. Preferably, the molecular complex shows at least 5, preferably at least 8 or at least 12, more preferably at least 15, even more preferably at least 20, or all of the reflexes shown in Table 3 as degree 2-Theta ($^{\circ}$ 2 θ) values $\pm$ 0.2 degrees 2-theta. The crystalline form may also be identified by its differential scanning calorimetry (DSC) curve as shown in Figure 6, in particular by the melting point temperature with an onset temperature of about 95.2 $^{\circ}$ C as determined by DSC.

In a further embodiment, the present invention relates to a molecular complex comprising, or consisting essentially of, dicamba and prometryn (6-methylsulfanyl-2-N,4-N-di(propan-2-yl)-1,3,5-triazine-2,4-diamine). The molar ratio of dicamba: prometryn is generally in the range from 1:1 to 2:1, such as 1:1. However, variations are possible which typically do not exceed 20 mol% and preferably do not exceed 10 mol%.

In the case that the molar ratio of dicamba: prometryn is 1:1, the current inventors have identified a crystalline form which exhibits an x-ray powder diffraction pattern (Cu K α radiation) substantially as shown in Figure 7. The XRPD degree 2-theta ($^{\circ}$ 2 θ) values are shown in Table 4. Preferably, the molecular complex shows at least 5, preferably at

least 8 or at least 12, more preferably at least 15, even more preferably at least 20, or all of the reflexes shown in Table 6 as degree 2-Theta ($^{\circ}$ 2 θ) values $\pm$ 0.2 degrees 2-theta. The crystalline form may also be identified by its differential scanning calorimetry (DSC) curve as shown in Figure 8, in particular by the melting point temperature with an onset temperature of about 127 $^{\circ}$ C as determined by DSC. The crystalline form may also be identified by single crystal x-ray crystallography. Preferably, the molecular complex has a unit cell, as determined by single crystal x-ray crystallography, of the following dimensions: $a = 14.32$ (4) $\text{\AA}$; $b = 11.97$ (3) $\text{\AA}$; $c = 14.47$ (4) $\text{\AA}$; $\alpha = 90^{\circ}$; $\beta = 117$ (3) $^{\circ}$; $\gamma = 90^{\circ}$, or a substantially as described in Table 6.

- 10 In a further embodiment, the present invention relates to a molecular complex comprising, or consisting essentially of, dicamba and ametryn (4-N-ethyl-6-methylsulfanyl-2-N-propan-2-yl-1,3,5-triazine-2,4-diamine). The molar ratio of dicamba: ametryn is generally in the range from 1:1 to 2:1, such as 1:1. However, variations are possible which typically do not exceed 20 mol% and preferably do not exceed 10 mol%.
- 15 In the case that the molar ratio of dicamba: ametryn is 1:1, the current inventors have identified a crystalline form which exhibits an x-ray powder diffraction pattern (Cu K α radiation) substantially as shown in Figure 9. The XRPD degree 2-theta ($^{\circ}$ 2 θ) values are shown in Table 7. Preferably, the molecular complex shows at least 5, preferably at least 8 or at least 12, more preferably at least 15, even more preferably at least 20, or all of the reflexes shown in Table 7 as degree 2-Theta (2 θ) values $\pm$ 0.2 degrees 2-theta. The crystalline form may also be identified by its differential scanning calorimetry (DSC) curve as shown in Figure 10, in particular by the melting point temperature with an onset temperature of about 116.7 $^{\circ}$ C as determined by DSC.

- 25 The molecular complexes may be formulated into a herbicidal composition with at least one agriculturally acceptable carrier. The composition may be a solid formulation, for example a powder, granule, or dust, or may be a liquid formulation, such as a suspension of particles of the molecular complex.

- In one embodiment, the herbicidal composition is an aqueous suspension concentrate, i.e. an aqueous composition comprising particles of the molecular complex dispersed in an aqueous medium.

In a further embodiment, the herbicidal composition is a suspo-emulsion, i.e. an aqueous composition comprising particles of the molecular complex dispersed in an aqueous medium and a water-immiscible organic solvent, optionally with one or more additional herbicides solubilised in the organic solvent.

In another embodiment, the herbicidal composition is a solid formulation, such a powder, for example a water-dispersible powder or a dustable powder, or a granulated composition, such as water-dispersible granules.

5 It will be understood by the skilled person that the compositions may also include further components, such as surfactants, viscosity modifiers, anti-freeze agents, agents for pH control, preservatives, stabilisers and anti-caking agents.

The amount of the molecular complex in the composition is generally between 0.001 and 99 wt%, such as between 1 and 99%, 5 and 95 wt% or 10 and 90 wt% based on the total weight of the composition.

10 In liquid compositions which are designed to be diluted prior to use, such as an aqueous suspension concentrate or a suspo-emulsion, the amount of molecular complex is typically in the range from 10 and 90 wt%, such as between 10 and 70 wt%, in particular in the range from 15 to 50 wt%, based on the total weight of the composition. Such compositions are then diluted, typically with water, to around 0.001 and 1 wt% of active
15 material before application.

In solid formulations, the amount of molecular complex is typically in the range from 10 to 90 wt%, in particular in the range from 15 to 70 wt%, based on the total weight of the composition.

The amount of carrier varies depending on the formulation type. Typically, the carrier is
20 in the range from 1 to 90 wt%, in particular from 30 to 90 wt%, or particularly preferably between 30 to 85 wt%, or 50 to 85 wt% based on the total weight of the composition.

Suitable agriculturally acceptable carriers are well known to those skilled in the art. Such carriers should not be phytotoxic to crops, in particular at the concentrations employed for the control of undesirable plants in the presence of crops and should not react
25 chemically with the compounds of the molecular complex or other composition components. The compositions may be applied directly, or may be formulations or concentrates which are diluted, for example with water, prior to application.

Liquid carriers that may be employed include water, optionally including water-miscible organic solvents, and organic solvents, although it is typically preferred that water is
30 used. If organic solvents are used, then it will be understood that the organic solvent or solvents should be selected in which the molecular complexes have low solubility, for examples solvents in which the solubility is less than 1 mg/ml at 25 °C.

Suitable solid carriers include mineral earths, such as clays, silicates, diatomaceous earths, or kaolin, fertilisers, and organic products such as woodmeal and cellulose carriers.

5 Generally, the solid and liquid compositions comprise the molecular complexes in finely divided particulate form. In liquid compositions, the particles of the molecular complex are suspended in a liquid medium, preferably in an aqueous medium. In water-dispersible granules or water-dispersible powders the finely divided particles are typically loosely agglomerated into larger granules that disintegrate upon dilution in water and then lead to a suspension of these finely divided particles. The size of the particles of the
10 molecular complex, i.e. the size which is not exceeded by 90% by weight of the active compound particles, is typically not more than 30 μm , preferably not more than 20 μm , in particular not more than 10 μm , especially not more than 5 μm , as determined by dynamic light scattering.

15 Suspension concentrates, in particular aqueous suspension concentrates, can be prepared by suspending particles of the molecular complex in a suitable liquid carrier. The suspension concentrate may also be prepared by mixing or milling particles of dicamba and the selected triazine herbicide in the liquid medium until a molecular complex has been formed.

20 Suspo-emulsions can be prepared in accordance with the method as described for suspension concentrates with the addition of an organic solvent, typically containing an additional active ingredient, such as a herbicide, pesticide or fungicide, to the formed suspension concentrate or during the preparation of the suspension concentrate.

Powders, such as dustable or water-dispersible powders, can be prepared by mixing or grinding particles of the molecular complex with a solid carrier.

25 Granules, for example water-dispersible granules, can be prepared by binding the particles of the molecular complex to suitable solid carriers.

The compositions as described above may also comprise further active compounds. For example, insecticides, fungicides, or further herbicides can be added as required.

30 All embodiments of the compositions comprising at least one molecular complex described herein are referred to as a "herbicidal composition".

The herbicidal compositions as described herein may be used for controlling undesirable vegetation. Undesirable vegetation is understood to mean plants considered undesirable in a particular location, e.g. in an area of crops, and may be known as weeds.

Control may be achieved by a method comprising contacting the vegetation with the herbicidal composition. It will be understood by the skilled person that the composition at the point of application should contain a herbicidally effective amount of the molecular complex. A herbicidally effective amount is an amount of the active ingredients which causes an adverse deviation of the natural development of the undesired vegetation.

In particular, the compositions have utility for controlling undesirable vegetation in a culture of crop plants, especially crop plants which are tolerant to dicamba and / or triazine herbicides, for example through genetic modification of the crop plants. The compositions may also have particular utility for the control of undesirable vegetation which is resistant to either dicamba and / or the selected triazine herbicide.

The present invention also comprises a method for the preparation of molecular complexes according to the present invention, the method comprising combining dicamba and the selected triazine herbicide in a suitable solvent.

In one embodiment of the process, dicamba and the triazine herbicide are dissolved in at least one solvent to form a solution, optionally with heating, and then crystallisation is induced, for example, by cooling the solution, evaporation of the solvent, or by precipitation. Precipitation may be induced, for example, by the addition of an anti-solvent or by cooling.

For example, in the case that the molecular complexes comprise dicamba and terbutryn, crystallisation may be achieved by the formation a solution of dicamba and terbutryn in a suitable solvent, such as ethanol, and then cooling the solution to induce precipitation of particles of the molecular complex, such as cooling to a temperature of around 5 °C.

In a further embodiment of the process, dicamba and the triazine herbicide are combined with a suitable solvent (e.g. heptane) but the compounds are not fully dissolved so that solid material remains. The mixture is then subjected to stirring, milling or grinding until the crystalline molecular complexes are obtained. The amount of time required for molecular complex formation can be readily determined by one skilled in the art and depends on factors including the temperature and the level of energy input.

For example, in the case that the molecular complexes comprise dicamba and atrazine, dicamba and ametryn, dicamba and prometryn, or dicamba and cyanazine, particles of the molecular complex may be formed by the combination of dicamba and the selected triazine with a suitable solvent, such as heptane, in an amount such that the compounds

are not fully dissolved, and then milling or mixing the mixture to form the desired crystalline product.

- It has been advantageously found that the molecular complexes may be formed by milling the active materials with a suitable solvent (e.g. heptane) to form a suspension of particles of the molecular complex. Such a method may simplify the manufacture of herbicidal compositions as described herein, in particular compositions provided in the form of a suspension concentrate. Therefore, in a further embodiment of the method, the method comprises the steps of (i) preparing a suspension of dicamba and a triazine herbicide in heptane solvent; (ii) milling the aqueous suspension.
- The present invention will now be described with reference to the following examples, which are provided to assist with understanding the present invention and are not intended to limit its scope.

Examples

Example 1 – dicamba: terbutryn (1:1) molecular complex

- Terbutryn (200 mg) (Bond Chemicals Ltd) and dicamba (VWR) (183 mg, 1 mol eq) were dissolved in ethanol (2 ml) at 50 °C with stirring. The clear solution was then cooled to 5 °C at 0.5 °Cmin⁻¹ and held for 4 hrs with stirring at 500 rpm. The suspension was filtered, then dried under suction.

- The formed material was analysed by XRPD which showed a crystalline material and yielded a diffractogram as provided in Figure 1.

Table 1 – Example 1 (1:1) XRPD peak table

Angle (2-Theta °)	Intensity (%)	Angle (2-Theta °)	Intensity (%)
7.6	38.9	22.6	8.5
9.9	17.4	23.0	18.2
10.6	52.5	23.5	27.9
13.0	6.8	24.5	86.7
14.4	45.8	24.9	14.6
14.8	48.1	25.3	11.6
15.3	31.8	25.6	10.5
16.9	23.8	25.9	22.5
18.0	8.0	26.9	15.8

Angle (2-Theta °)	Intensity (%)	Angle (2-Theta °)	Intensity (%)
19.1	25.5	28.1	14.8
19.5	44.4	28.6	16.2
19.7	24.3	29.6	14.4
20.9	18.7	30.3	14.3
21.2	100.0	31.0	11.3
21.4	48.4	32.0	14.6
21.6	27.4	33.5	10.6

DSC analysis (Figure 2) indicated a melting point with an onset temperature of about 124.3 °C.

Example 2 - dicamba: atrazine (1:1) molecular complex

- 5 Atrazine (20 mg) (Tokyo Chemical Industry) and dicamba (21 mg) (VWR) were placed in a 2 ml HPLC vial with two grinding beads. The mixture was initially wetted with heptane (10 µl) and ground for 2 hrs at 600 rpm using a Fritsch milling system with an Automaxion adapter then air dried for 5 min.

The formed material was analysed by XRPD which showed a crystalline material and
 10 yielded a diffractogram as provided in Figure 3.

Table 2 – Example 2 (1:1) XRPD peak table

Angle (2-Theta °)	Intensity (%)	Angle (2-Theta °)	Intensity (%)
5.3	46.7	19.7	20.6
9.0	22.1	20.0	30.4
10.3	48.2	20.2	44.5
10.5	44.5	20.7	15.8
11.0	17.4	21.3	54.8
11.5	29.2	22.0	40.4
11.9	15.5	22.4	24.3
12.7	100.0	22.7	17.4
13.1	21.3	23.2	46.5
14.2	35.8	23.4	37.5

Angle (2-Theta °)	Intensity (%)	Angle (2-Theta °)	Intensity (%)
15.8	28.1	23.6	25.9
16.1	18.2	23.9	19.9
16.6	18.8	24.7	14.7
16.8	24.6	25.0	19.5
17.5	13.5	25.4	27.6
17.8	24.4	26.5	21.7
18.2	47.9	26.9	17.3
18.7	14.8	28.1	17.2
19.0	13.7	28.8	18.8
19.4	31.1	29.1	23.6

DSC analysis Figure 4 indicated a melting point with an onset temperature of about 81.6 °C.

Example 3 - Dicamba: cyanazine (1:1) molecular complex

- 5 A slurry of cyanazine (20 mg) (Bond Chemicals Ltd) and dicamba (18 mg) (VWR) was stirred at 600 rpm, at 50 °C for 48 hrs in heptane (1 ml). The slurry was filtered and dried under suction.

The formed material was analysed by XRPD which showed a crystalline material and yielded a diffractogram as provided in Figure 5.

10

Table 3 – Example 3 (1:1) XRPD peak table

Angle (2-Theta °)	Intensity (%)
9.5	100.0
13.9	6.0
15.7	5.9
16.0	2.7
17.6	2.2
19.1	1.9
20.1	1.9
21.0	1.8

Angle (2-Theta °)	Intensity (%)
21.2	6.3
21.8	8.4
22.8	3.5
23.1	10.1
24.3	4.9
24.5	7.3
25.3	2.4
26.6	4.9
27.3	4.1
28.3	3.2
28.8	2.1
29.9	3.4
31.0	2.9

DSC analysis Figure 6 indicated a melting point with an onset temperature of about 95.2 °C.

Example 4 - dicamba: prometryn (1:1) molecular complex

- 5 A slurry of prometryn (20 mg) (Bond Chemicals Ltd) and dicamba (18 mg) (VWR) was stirred at 600 rpm, at 50 °C for 48 hrs in heptane (1 ml). The slurry was filtered and dried under suction.

The formed material was analysed by XRPD which showed a crystalline material and yielded a diffractogram as provided in Figure 7.

- 10 Table 4 – Example 4 (1:1) XRPD peak table

Angle (2-Theta °)	Intensity (%)	Angle (2-Theta °)	Intensity (%)
7.1	33.7	24.6	10.1
10.0	25.2	25.5	18.8
10.2	15.9	25.7	10.0
13.7	19.3	26.1	9.2
14.2	100.0	26.7	5.9
14.8	5.3	28.5	5.7

Angle (2-Theta °)	Intensity (%)	Angle (2-Theta °)	Intensity (%)
15.5	32.8	29.0	7.5
16.0	62.4	29.2	8.3
16.3	5.3	29.5	6.9
18.4	6.5	30.6	12.4
18.9	3.3	30.9	13.3
19.1	11.8	31.4	6.6
19.4	6.0	32.2	6.7
19.8	56.5	33.3	5.0
20.1	25.7	33.6	5.3
20.5	5.5	34.1	4.8
21.3	18.4	34.4	5.4
21.8	15.4	35.3	4.8
23.2	31.8	36.4	3.8
23.7	37.3	38.1	8.4
23.9	59.4	39.9	6.3
24.3	59.0	41.8	6.4

DSC analysis Figure 8 indicated a melting point with an onset temperature of about 127.0 °C.

The sample was further analysed by single crystal x-ray crystallography to determine the
 5 crystal structure as follows:

Table 5. Example 4 (1:1) single crystal data collection and structure refinement parameters

5	Diffractometer	SuperNova, Dual, Cu at zero, Atlas
	Radiation source	SuperNova (Cu) X-ray Source, CuK α
	Data collection method	omega scans
	Theta range for data collection	3.599 to 70.131°
	Index ranges	$-17 \leq h \leq 17, -14 \leq k \leq 14, -17 \leq l \leq 17$
10	Reflections collected	21552
	Independent reflections	4189 [R(int) = 0.0372]
	Coverage of independent reflections	100.0 %
	Variation in check reflections	n/a
	Absorption correction	Semi-empirical from equivalents
15	Max. and min. transmission	1.00000 and 0.75559
	Structure solution technique	Direct methods
	Structure solution program	SHELXTL (Sheldrick, 2013)
	Refinement technique	Full-matrix least-squares on F^2
	Refinement program	SHELXL-2013 (Sheldrick, 2013)
20	Function minimized	$\sum w(F_o^2 - F_c^2)^2$
	Data / restraints / parameters	4189 / 0 / 280
	Goodness-of-fit on F^2	1.059
	$\Delta/\sigma_{\max}$	0.000
	Final R indices	
25	3742 data; $I > 2 \sigma(I)$	R1 = 0.0335, wR2 = 0.0833
	all data	R1 = 0.0392, wR2 = 0.0877
	Weighting scheme	$w = 1 / [\sigma^2(F_o^2) + (0.0450P)^2 + 1.2994P]$ where $P = (F_o^2 - 2F_c^2)/3$
	Extinction coefficient	n/a
30	Largest diff. peak and hole	0.512 and -0.242 eÅ ⁻³

Table 6. Example 4 (1:1) molecular complex single crystal structure parameters

5	Compound number	Prometryn: dicamba 1:1
	Crystallisation solvents	Acetone
	Crystallisation method	Evaporation
	Empirical formula	C ₁₈ H ₂₅ Cl ₂ N ₅ O ₃ S
	Formula weight	462.39
10	Temperature	100(2) K
	Wavelength	1.54184 Å
	Crystal size	0.35 x 0.20 x 0.13 mm
	Crystal habit	colourless prism
	Crystal system	Monoclinic
15	Space group	<i>P</i> 2 ₁ / <i>n</i>
	Unit cell dimensions	<i>a</i> = 14.3160(4) Å $\alpha = 90^\circ$ <i>b</i> = 11.9680(3) Å $\beta = 117.147(3)^\circ$ <i>c</i> = 14.4684(4) Å $\gamma = 90^\circ$
	Volume	2205.84(11) Å ³
20	Z	4
	Density (calculated)	1.392 Mg/m ³
	Absorption coefficient	3.783 mm ⁻¹
	<i>F</i> (000)	968

25

Example 5 - dicamba: ametryn (1:1)

A slurry of ametryn (20 mg) (Bond Chemicals Ltd) and dicamba (19 mg) (VWR) were stirred at 600 rpm, at 50 °C for 48 hrs in heptane (1 ml). The slurry was filtered and dried under suction.

30 The formed material was analysed by XRPD which showed a crystalline material and yielded a diffractogram as provided in Figure 9.

Table 7 – Example 5 (1:1) XRPD peak table

Angle (2-Theta °)	Intensity (%)	Angle (2-Theta °)	Intensity (%)
7.2	96.8	23.7	68.3
10.1	36.3	24.1	96.8
10.3	27.5	24.3	30.1
13.8	36.0	24.6	45.9
14.3	73.9	24.9	76.4
14.5	100.0	25.5	23.4
15.5	61.9	25.7	28.5
15.6	46.1	27.3	17.3
16.2	71.7	28.6	17.9
18.8	34.7	29.3	16.0
19.3	29.6	30.5	19.2
19.9	27.5	31.3	25.6
20.1	91.2	31.7	15.0
20.4	31.7	32.2	24.5
20.6	25.4	34.8	18.1
21.8	22.1	35.7	15.5
22.0	17.9	38.3	20.3
23.2	57.9		

DSC analysis Figure 10 indicated a melting point with an onset temperature of about
5 116.7 °C.

Molecular complex testing

X-Ray Powder Diffraction (XRPD)

XRPD diffractograms were collected on a Bruker D8 Advance diffractometer.

Bruker D8 uses Cu K α radiation (40 kV, 40 mA) and a θ -2 θ goniometer fitted with a
10 Ge monochromator. The incident beam passes through a 2.0 mm divergence slit followed
by a 0.2 mm anti-scatter slit and knife edge. The diffracted beam passes through an
8.0 mm receiving slit with 2.5° Soller slits followed by the Lynxeye Detector. The software

used for data collection and analysis was Diffrac *Plus* XRD Commander and Diffrac *Plus* EVA respectively.

5 Samples were run under ambient conditions as flat plate specimens using powder as received. The sample was prepared on a polished, zero-background (510) silicon wafer by gently pressing onto the flat surface or packed into a cut cavity. The sample was rotated in its own plane.

Data collection method for examples 1, 3 and 4 is:

- Angular range: 2 to 42° 2 θ
- Step size: 0.05° 2 θ
- 10 • Collection time: 0.5 s/step

Data collection method for examples 2 and 5 is:

- Angular range: 4 to 30° 2 θ
- Step size: 0.05° 2 θ
- Collection time: 4 s/step

15 **Thermodynamic solubility in water**

Aqueous solubility was determined by suspending sufficient amount of compound in deionised water to give a maximum final concentration of ≥ 10 mg/ml of the compound. The suspension was equilibrated at 25 °C, on a Heidolph plate shaker set to 750 rpm for 24 hrs. The pH of the saturated solution was then measured, and the suspension filtered through
20 a glass fibre C filter (particle retention 1.2 μ m) and diluted appropriately. Quantitation was by HPLC with reference to a standard solution of approximately 0.15 mg/ml in DMSO. Different volumes of the standard, diluted and undiluted sample solutions were injected. The solubility was calculated using the peak areas determined by integration of the peak found at the same retention time as the principal peak in the standard injection.

25 Analysis was performed on an Agilent HP1100 series system equipped with a diode array detector and using ChemStation software.

Table 8 - HPLC method for solubility measurements

Parameter	Value		
Type of method	Reverse phase with gradient elution		
Column	Phenomenex Luna, C18 (2) 5 mm 50 x 4.6 mm		
Column Temperature (°C)	25		
Standard Injections (ml)	1, 2, 3, 4, 5, 7		
Test Injections (ml)	1, 2, 3, 10, 15, 20		
Detection:	260,90		
Wavelength, Bandwidth (nm)			
Flow Rate (ml/min)	2		
Phase A	0.1% TFA in water		
Phase B	0.085% TFA in acetonitrile		
Timetable	Time (min)	% Phase A	% Phase B
	0	95	5
	1	80	20
	2.3	5	95
	3.3	5	95
	3.5	95	5
	4.4	95	5

Volatility

- 5 Volatility data were collected on a TA Instruments Discovery TGA, equipped with a 25-position auto-sampler. Typically, >5 mg, to cover the surface of the pan of each sample was loaded onto a pre-tared aluminium pan (6.5 mm diameter) and heated at 10 °C/min from ambient temperature to 70 °C then held for 12 hrs. A nitrogen purge at 25 ml/min was maintained over the sample. Volatility is calculated by measuring the weight loss between
- 10 two time points once a steady state has been achieved, typically separated by 300-400 minutes, then dividing the weight loss by the time difference to get mg/min.

Differential Scanning calorimetry (DSC)

DSC (melting point) was assessed using either a TA Instruments Q2000 or TA Instruments Discovery DSC. Typically, 0.5 – 3 mg of each sample, in a pin-holed aluminium pan, was

heated at 10 °C/min from 25 °C to 300 °C. A purge of dry nitrogen at 50 ml/min was maintained over the sample.

Example 1

- 5 The physicochemical properties of the dicamba: terbutryn molecular complex formed in Example 1 were tested alongside the individual compounds dicamba and terbutryn. The results are provided in Table 9.

Table 9 – Results of the testing of physicochemical properties of the molecular complex formed in Example 1

Technique	Example 1	Terbutryn	Dicamba
Thermodynamic solubility in water (25 °C) (pH)	Dicamba 0.28 mg/ml Terbutryn 0.1 mg/ml (3.57)	0.03 mg/ml (8.85)	4.33 mg/ml (1.9)
Volatility (mg/min)	3.2E-05	1.5 E-4	3.01E-04
DSC (melting point)	124.3 °C	102.2 °C	113.6 °C

10

Example 2

The physicochemical properties of the dicamba: atrazine molecular complex formed in Example 2 were tested alongside the individual compounds dicamba and atrazine. The results are provided in Table 10.

- 15 Table 10 – Results of the testing of physicochemical properties of the molecular complex formed in Example 2

Technique	Example 2	Atrazine	Dicamba
Volatility (mg/min)	5.2E-04	2.94E-05	3.01E-04
DSC (melting point)	81.6 °C	176.0 °C	113.6 °C

Example 3

The physicochemical properties of the dicamba: cyanazine molecular complex formed in Example 3 were tested alongside the individual compounds dicamba and cyanazine. The results are provided in Table 11.

5

Table 11 – Results of the testing of physicochemical properties of the molecular complex formed in Example 3

Technique	Example 3	Cyanazine	Dicamba
Thermodynamic solubility in water (25 °C) (pH)	Dicamba 1.2 mg/ml Cyanazine 0.6 mg/ml (2.38)	0.02 mg/ml (7.39)	4.33 mg/ml (1.9)
Volatility (mg/min)	4.4E-04	1.5E-06	3.01E-04
DSC (melting point)	95.2 °C	164.3 °C	113.6 °C

Example 4

10

The physicochemical properties of the dicamba: prometryn molecular complex formed in Example 4 were tested alongside the individual compounds dicamba and prometryn. The results are provided in Table 12.

Table 12 – Results of the testing of physicochemical properties of the molecular complex formed in Example 4

Technique	Example 4	Prometryn	Dicamba
Thermodynamic solubility in water (25 °C) (pH)	Dicamba 0.27 mg/ml Prometryn 0.05 mg/ml (3.37)	0.03 mg/ml (8.99)	4.33 mg/ml (1.9)
Volatility (mg/min)	3.1E-05	8.3 E-5	3.01E-04
DSC (melting point)	127.0 °C	119.5 °C	113.6 °C

Example 5

15

The physicochemical properties of the dicamba: ametryn molecular complex formed in Example 5 were tested alongside the individual compounds dicamba and ametryn. The results are provided in Table 13.

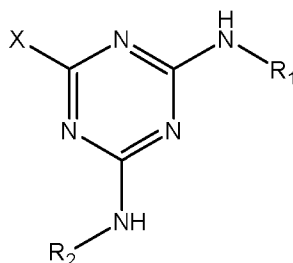
Table 13 – Results of the testing of physicochemical properties of the molecular complex formed in Example 5

Technique	Example 5	Ametryn	Dicamba
Thermodynamic solubility in water (25 °C) (pH)	Dicamba 0.44 mg/ml Ametryn 0.41 mg/ml (2.0)	0.20 mg/ml (8.99)	4.33 mg/ml (1.9)
Volatility (mg/min)	3.0E-5	9.5 E-5	3.01E-04
DSC (melting point)	116.7 °C	85.0 °C	113.6 °C

- The information from the analysis of physiochemical properties of the crystalline materials shows that the formation of molecular complexes provides the active ingredients in a form in which the aqueous solubilities are closely matched (with a reduction in dicamba solubility). Furthermore, formation of molecular complexes can provide dicamba in a form with reduced volatility.

Claims

1. A molecular complex comprising:
3,6-dichloro-2-methoxybenzoic acid (dicamba); and
a compound selected from the group of triazine herbicides.
2. A molecular complex according to claim 1 wherein the triazine herbicide is of formula (I):



(I)

- wherein X = Cl, -OCH₃, or -SCH₃; R₁ = ethyl or isopropyl; R₂ = ethyl, iso-propyl, cyclopropyl, tert-butyl, or -C(CH₃)₂CN.
3. A molecular complex according to claim 1 or claim 2 wherein the molar ratio of dicamba to the triazine herbicide is 1:1.
 4. A molecular complex according to any one of the preceding claims wherein the triazine herbicide is selected from atrazine, cyanazine, terbutryn, prometryn or ametryn.
 5. A molecular complex according to any one of the preceding claims wherein the triazine herbicide is terbutryn.
 6. A molecular complex according to claim 5 wherein the molar ratio of dicamba: terbutryn is 1:1.
 7. A molecular complex according to claim 5 or claim 6 wherein an X-ray powder diffractogram shows at least five of the following diffraction lines: 7.6, 9.9, 10.6, 13.0, 14.4, 14.8, 15.3, 16.9, 18.0, 19.1, 19.5, 19.7, 20.9, 21.2, 21.4, 21.6, 22.6, 23.0, 23.5, 24.5, 24.9, 25.3, 25.6, 25.9, 26.9, 28.1, 28.6, 29.6, 30.3, 31.0, 32.0, 33.5 degrees two-theta ± 0.2 degrees 2-theta.
 8. A molecular complex according to claim 5 or claim 6 with a melting point with an onset temperature of about 124 °C.

9. A molecular complex according to any one of the preceding claims wherein the triazine herbicide is atrazine.
10. A molecular complex according to claim 9 wherein the molar ratio of dicamba: atrazine is 1:1.
- 5 11. A molecular complex according to claim 9 or claim 10 wherein an X-ray powder diffractogram shows at least five of the following diffraction lines: 5.3, 9.0, 10.3, 10.5, 11.0, 11.5, 11.9, 12.7, 13.1, 14.2, 15.8, 16.1, 16.6, 16.8, 17.5, 17.8, 18.2, 18.7, 19.0, 19.4, 19.7, 20.0, 20.2, 20.7, 21.3, 22.0, 22.4, 22.7, 23.2, 23.4, 23.6, 23.9, 24.7, 25.0, 25.4, 26.5, 26.9, 28.1, 28.8, 29.1 degrees two-theta $\pm$ 0.2 degrees 2-theta.
- 10 12. A molecular complex according to claim 9 or claim 10 with a melting point with an onset temperature of about 82 °C.
13. A molecular complex according to any one of claims 1 to 4 wherein the triazine herbicide is cyanazine.
14. A molecular complex according to claim 13 wherein the molar ratio of dicamba: cyanazine is 1:1.
- 15 15. A molecular complex according to claim 13 or claim 14 wherein an X-ray powder diffractogram shows at least five of the following diffraction lines: 9.5, 13.9, 15.7, 16.0, 17.6, 19.1, 20.1, 21.0, 21.2, 21.8, 22.8, 23.1, 24.3, 24.5, 25.3, 26.6, 27.3, 28.3, 28.8, 29.9, 31.0 degrees two-theta $\pm$ 0.2 degrees 2-theta.
- 20 16. A molecular complex according to claim 13 or claim 14 with a melting point with an onset temperature of about 95 °C.
17. A molecular complex according to any one of claims 1 to 4 wherein the triazine herbicide is prometryn.
18. A molecular complex according to claim 17 wherein the molar ratio of dicamba: prometryn is 1:1.
- 25 19. A molecular complex according to claim 17 or claim 18 wherein an X-ray powder diffractogram shows at least five of the following diffraction lines: 7.1, 10.0, 10.2, 13.7, 14.2, 14.8, 15.5, 16.0, 16.3, 18.4, 18.9, 19.1, 19.4, 19.8, 20.1, 20.5, 21.3, 21.8, 23.2, 23.7, 23.9, 24.3, 24.6, 25.5, 25.7, 26.1, 26.7, 28.5, 29.0, 29.2, 29.5, 30.6, 30.9, 31.4, 32.2, 33.3, 33.6, 34.1, 34.4, 35.3, 36.4, 38.1, 39.9, 41.8 degrees two-theta $\pm$ 0.2 degrees 2-theta.
- 30

20. A molecular complex according to claim 17 or claim 18 with a melting point with an onset temperature of about 127 °C.
21. A molecular complex according to claim 17 or claim 18 wherein the crystalline form has a unit cell, as determined by crystal x-ray crystallography, of the following
5 dimensions: $a = 14.32$ (4) Å; $b = 11.97$ (3) Å; $c = 14.47$ (4) Å; $\alpha = 90^\circ$; $\beta = 117$ (3)°; $\gamma = 90^\circ$.
22. A molecular complex according to any one of claims 1 to 4 wherein the triazine herbicide is ametryn.
23. A molecular complex according to claim 22 wherein the molar ratio of dicamba:
10 ametryn is 1:1.
24. A molecular complex according to claim 22 or claim 23 wherein an X-ray powder diffractogram shows at least five of the following diffraction lines: 7.2, 10.1, 10.3, 13.8, 14.3, 14.5, 15.5, 15.6, 16.2, 18.8, 19.3, 19.9, 20.1, 20.4, 20.6, 21.8, 22.0, 23.2, 23.7, 24.1, 24.3, 24.6, 24.9, 25.5, 25.7, 27.3, 28.6, 29.3, 30.5, 31.3, 31.7, 32.2, 34.8, 35.7, 38.3
15 degrees two-theta $\pm$ 0.2 degrees 2-theta.
25. A molecular complex according to claim 22 or claim 23 with a melting point with an onset temperature of about 117 °C.
26. A method of preparing a molecular complex according to any one of the preceding claims, which comprises combining dicamba and a triazine herbicide in a
20 suitable solvent.
27. A method according to claim 26 comprising the steps of:
- (i) preparing an aqueous suspension of dicamba and a triazine herbicide;
 - (ii) milling the aqueous suspension.
28. A herbicidal composition comprising a molecular complex according to any one of
25 claims 1 to 25 and at least one agriculturally acceptable carrier.
29. A herbicidal composition according to claim 28 wherein the composition is a solid formulation, such as a powder or granulated composition.
30. A herbicidal composition according to claim 28 wherein the composition is a liquid formulation, such as an aqueous suspension concentrate or a suspo-emulsion.

31. A herbicidal composition according to any one of claims 28 to 30 wherein the composition comprises between 10 and 90 wt% of the molecular complex based on the total weight of the composition.
32. The use of an herbicidal composition according to any one of claims 28 to 31 for
5 controlling undesired vegetation.
33. A method for controlling undesired vegetation comprising contacting the vegetation with a herbicidal composition according to any one of claims 28 to 31.

Figure 1

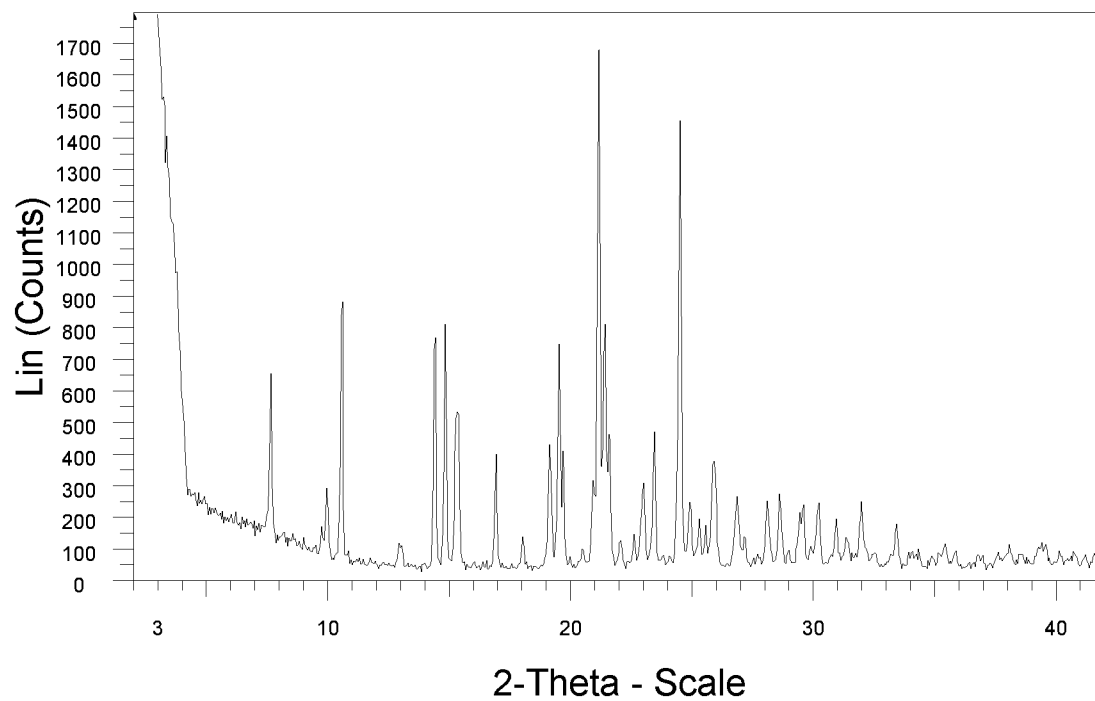


Figure 2

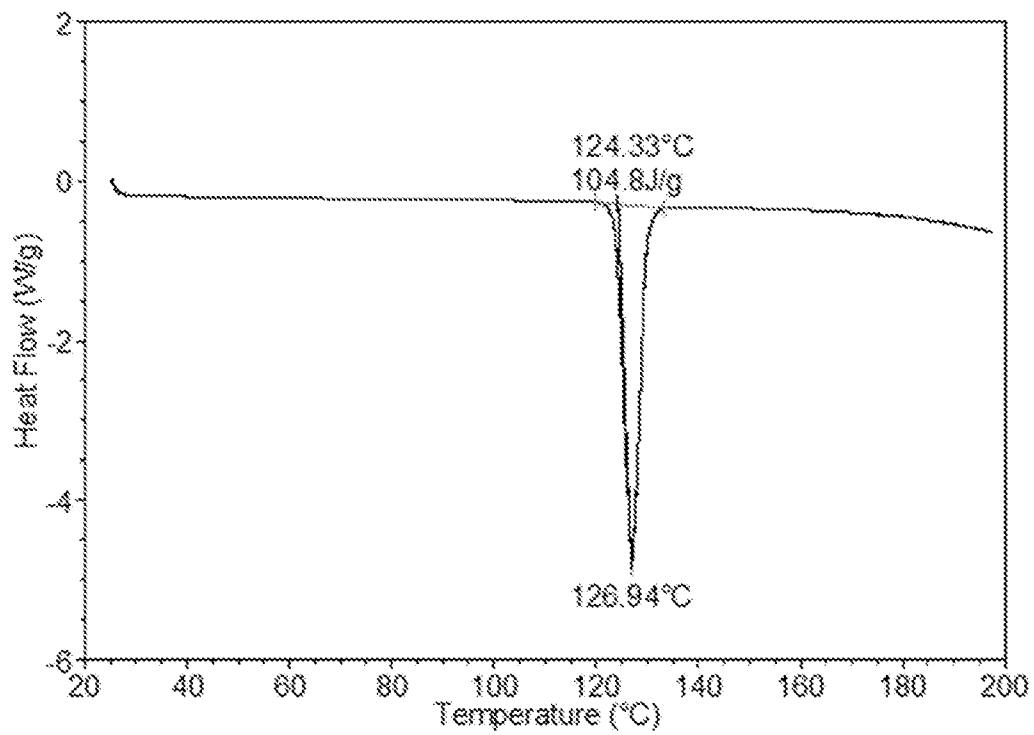


Figure 3

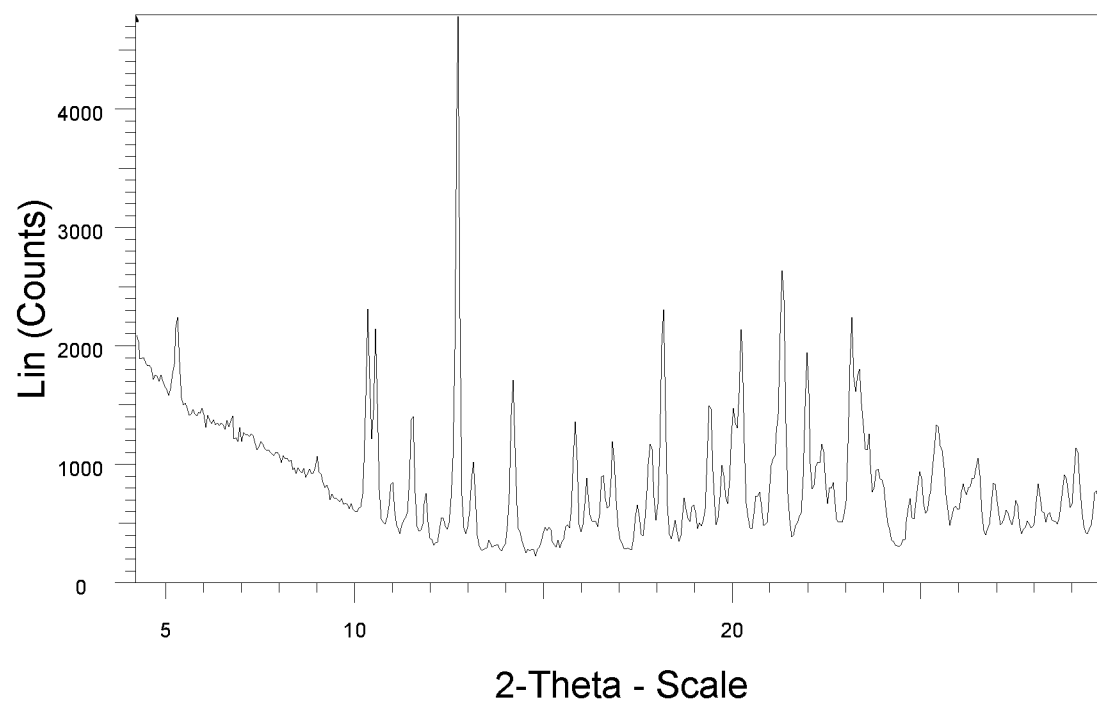


Figure 4

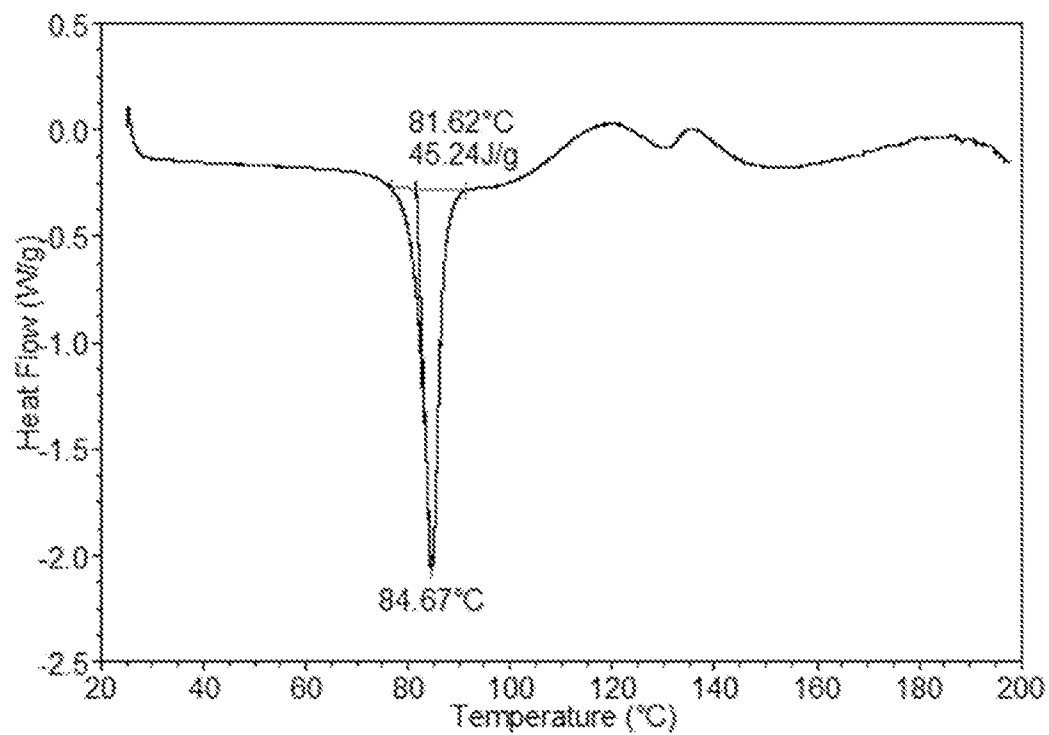


Figure 5

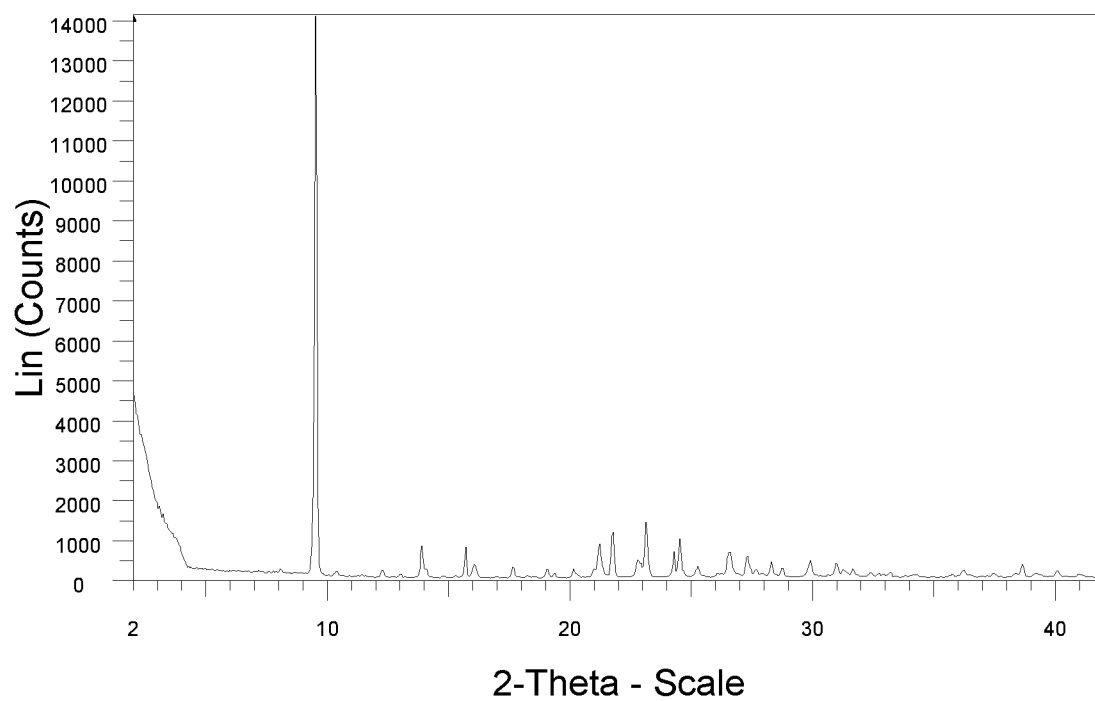


Figure 6

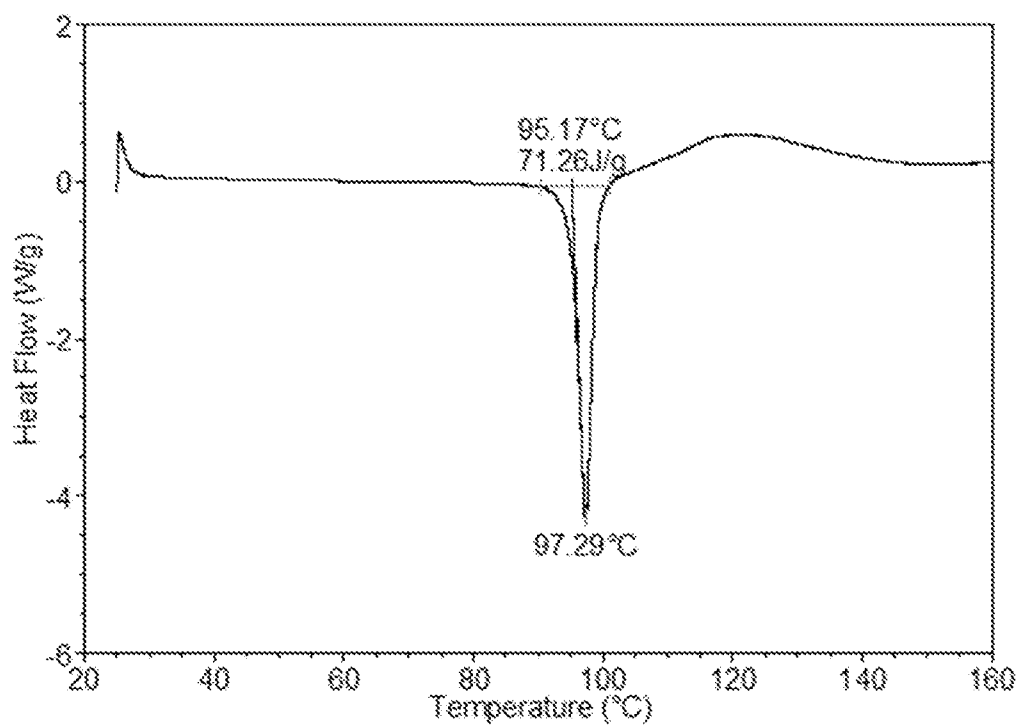


Figure 7

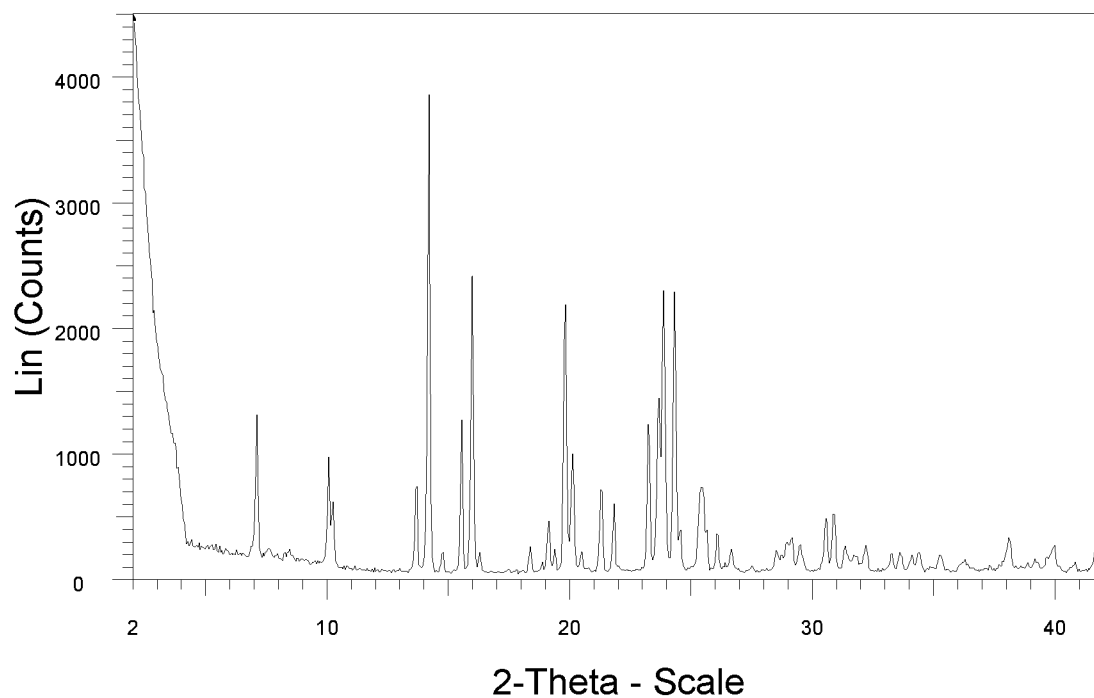


Figure 8

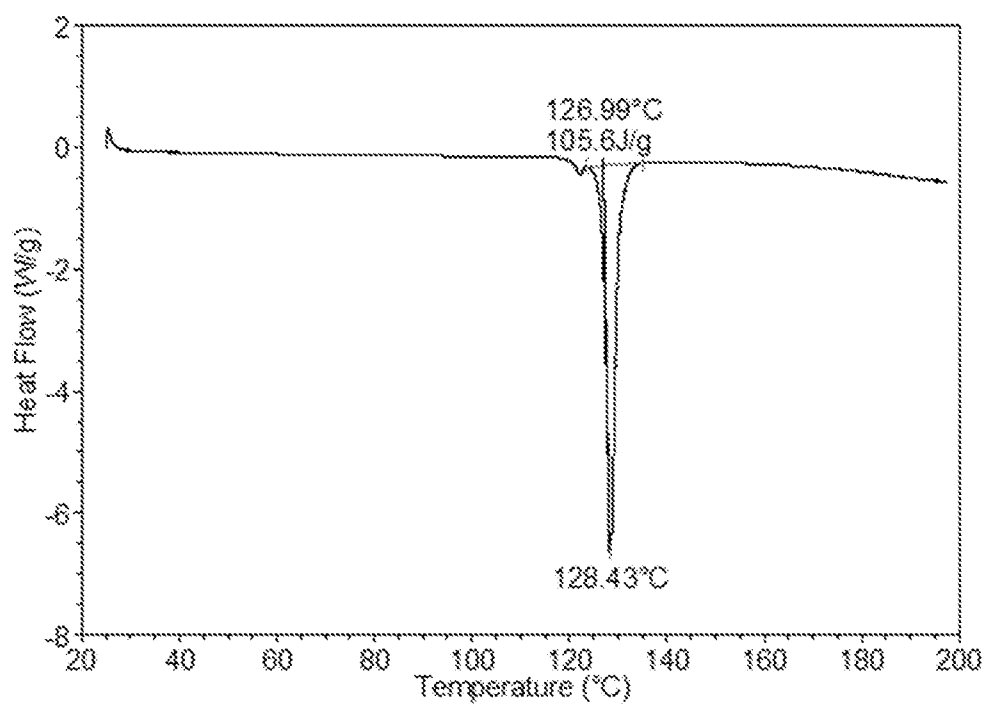


Figure 9

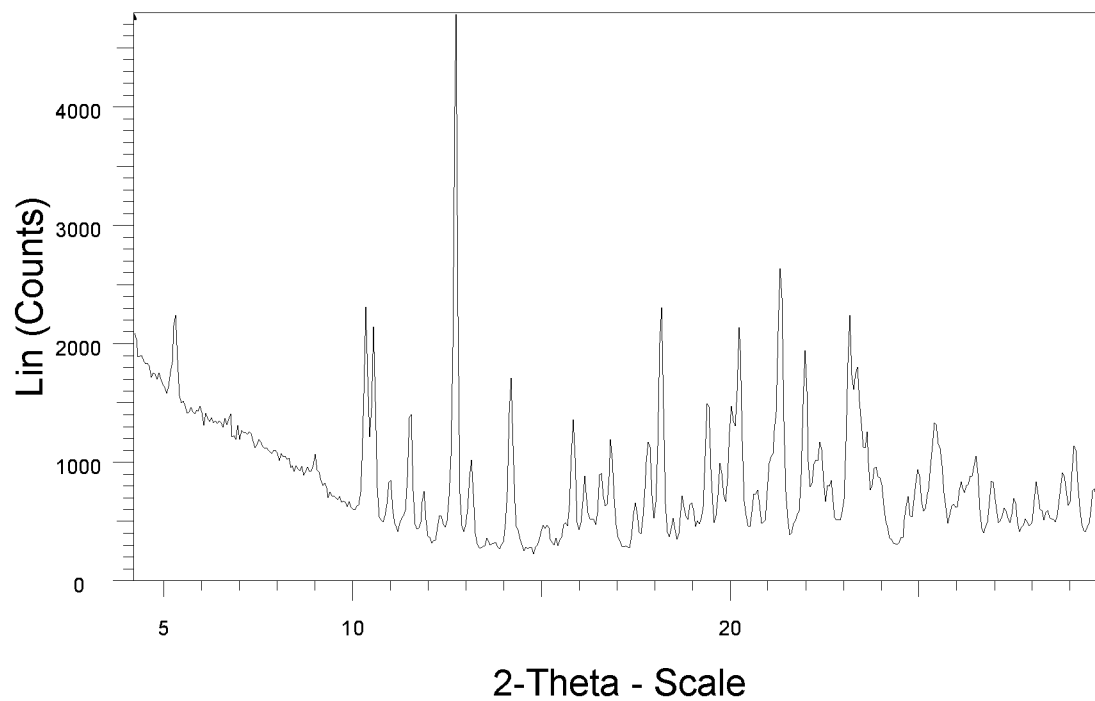


Figure 10

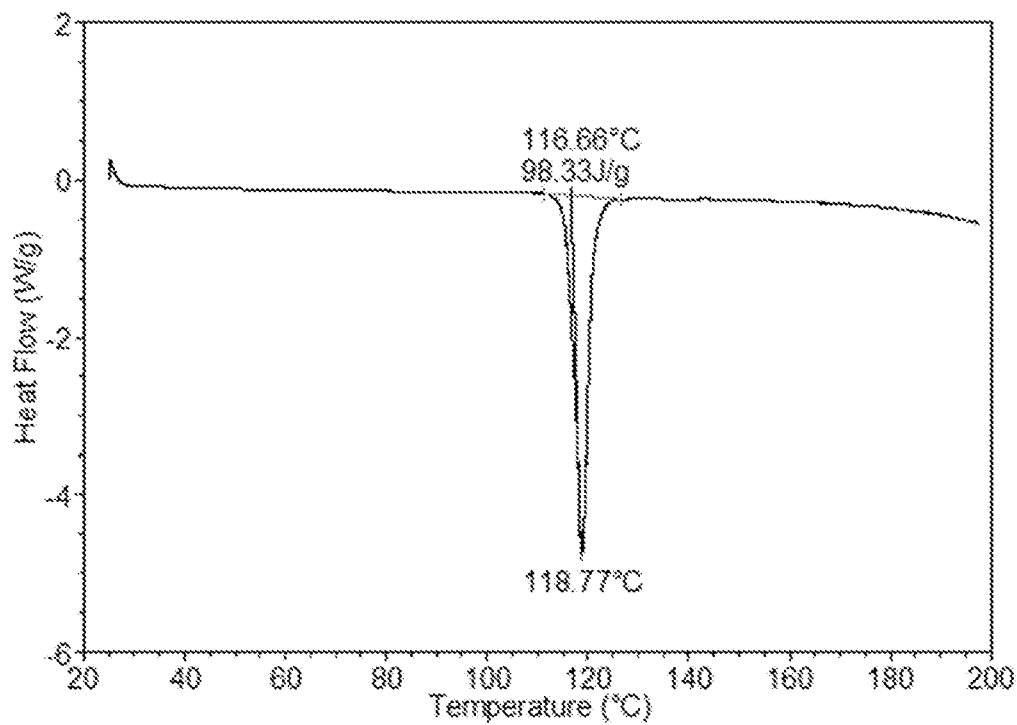
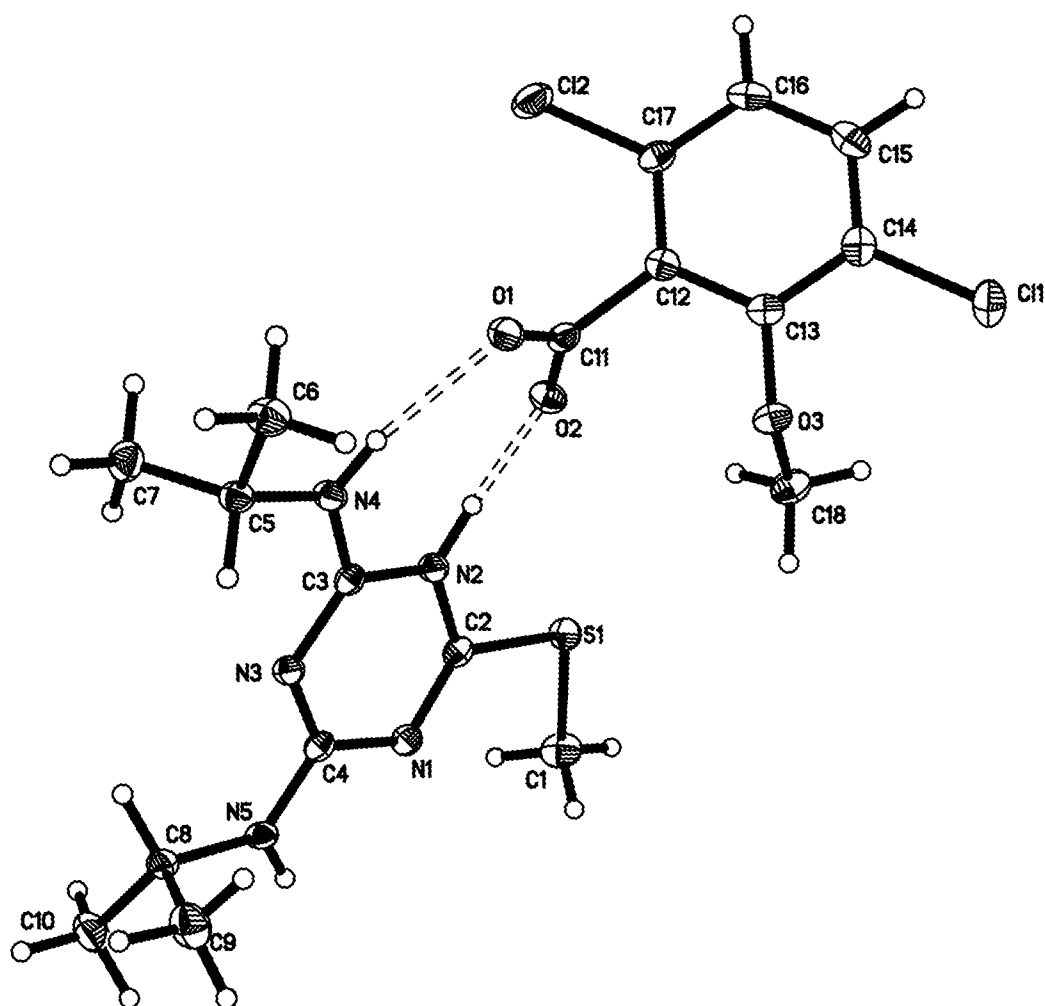


Figure 11



INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2019/052218

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07D251/50 C07D251/52 C07C65/21 A01N39/04 A01N43/70
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07D C07C A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 1 329 306 A (GEIGY AG J R) 7 June 1963 (1963-06-07) the whole document	1-6, 8-14, 16-18, 20,22, 24-32
X	WO 2013/143927 A1 (BASF SE [DE]; BASF SCHWEIZ AG [CH]) 3 October 2013 (2013-10-03) page 4, line 20 - line 23; claim 1; table 11	1-6, 8-14, 16-18, 20,22, 24-30



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

10 October 2019

Date of mailing of the international search report

23/10/2019

Name and mailing address of the ISA/

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Authorized officer

Johnson, Claire

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2019/052218

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1-6, 8-10, 12-14, 16-18, 20-22, 24-32(all partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1-6, 8-10, 12-14, 16-18, 20-22, 24-32(all partially)

According to p. 4, a molecular complex is a crystalline material. This feature is not present in claims 1-6, 8-10, 12-14, 16-18, 20, 21b, 22, 24-32. However, as mixtures of dicamba with triazine herbicides are well-known in the prior art, the present opinion is given for claims 1-32 only in so far as the molecular complex is a crystalline material.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2019/052218

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
FR 1329306	A	07-06-1963	BE	620373 A		10-10-2019
			FR	1329306 A		07-06-1963
			NL	281108 A		10-10-2019

WO 2013143927	A1	03-10-2013	AR	090564 A1		19-11-2014
			AU	2013242103 A1		16-10-2014
			CA	2867504 A1		03-10-2013
			EP	2830420 A1		04-02-2015
			US	2015065347 A1		05-03-2015
			WO	2013143927 A1		03-10-2013
