A critical and comparative study of recently collected specimens (available at CSIR-NBRI Herbarium (LWG)) with type specimens and description revealed that thalli are less wide at apex in our specimens compared to type specimens, i.e. 6–11(13) mm wide at apex and smaller size of pseudoelaters compared to type specimens (139–190 μm long), which may be due to changes in climatic and ecological conditions over a long period of time. *A. macrosporus* resembles *A. punctatus* L., *A. pandei* Udar & A. K. Asthana and *A. crectus* Kashyap in some features, especially the morphoform of thalli, but can be clearly recognized by its characteristic sporoderm architecture. In *A. punctatus* sporoderm is reticulate, rather pitted; *A. pandei* is clearly distinctive in having smaller spores (39–45 μm) with verrucate to lamellate sculpturing, while *A. erectus* can be distinguished by reticulate sporoderm pattern with spinulate ridges enclosing irregularly shaped lumeni.

Of the seven locations (five in Maharashtra and one each in Tamil Nadu and Gujarat) where *A. macrosporus* has been located in the country so far, the species could never be collected again from its type locality at Borghat in Maharashtra and Kodaikanal in Tamil Nadu. As such, the species is presently known from severely fragmented populations at only five inferred sites spread across Maharashtra and Gujarat with an 'extent of occurrence' of much less than 5000 km^2 and a highly restricted 'area of occupancy'. Therefore, as per the IUCN Red List categories and criteria version 3.1 (ref. 6), *A. macrosporus* belongs to endangered category [ENB1a + 2a; C2a(i)] at global level.

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Sodium bicarbonate aqueous matrix as novel industrial solvent for benzoylation of some Ar-OH, Ar-NH and R-HN functionalities

It is a well accepted fact that chemical transformations can occur in solid, liquid and gaseous matrix; however, liquid matrix (solvent) dominates due to certain distinct multi-dimensional advantages especially at molecular level, making it a versatile tool for industrial manufacturing processes[1–4]. It has been estimated that 28-million metric tonnes (MMT) of organic solvents are commercialized globally for different industrial purposes, majority of which get utilized in chemical and pharmaceutical manufacturing[5]. Recently, global regulatory pressure regarding toxicity of organic solvents on the living population[6] and their not ecofriendly characteristic[7], have raised significant concern worldwide to search for an alternatively less hazardous industrial solvent/s benign not only for the living population, but also ecologically compatible, chemically recyclable, and within the guideline of regulating authorities. 'Solvent substitution', is a newer philosophy currently adopted by most of the chemical manufacturing industries where manufacturing processes have now been shifted from conventional to less hazardous solvents without compromising on the final product both in terms of quality as well as quantity. Evaluation and in-process acceptance of newer solvent/s for classical manufacturing process is based on a thorough multi-dimensional assessment of the same by centralizing three main aspects: worker safety, process safety, and regulatory and environmental safety[8,9].

Benzoylation[10], a common substitution reaction involves introduction of ArCO-functionality (Scheme 1) into an organic compound. The technique is considered to be an economic, efficient, and feasible methodology for protecting and identifying aliphatic as well as aromatic organic

$$\begin{array}{lcl} \text{Ar-X + Ar}'\text{COCl} & \xrightarrow[\text{Stir 30–25 min}]{\text{NaOH (10\%)}} & \text{Ar-Y-COAr}' + \text{HCl} \\ \text{X-NH}_2 & & \text{Y-NH} \\ \text{X-OH} & \text{RT} & \text{Y-O} \end{array}$$

Scheme 1. Generalized depiction of benzoylation in NaOH to yield amide/ester derivatives.

Table 1. Physico-chemical characteristics of synthesized compounds

Host reactants/ moles	Benzoylating agent/ moles*	Solvent/quantity	Product	Reaction time (min)/ temperature	Melting point (°C) R^{18}	Melting point (°C) F	Yield (%)
Aniline/0.01M	Benzoyl chloride (0.01M)	Sodium bicarbonate (10 ml; 10%)	Benzanilide (**1a**)	01/RT	162	163	91
Phenol/0.01M	Benzoyl chloride (0.01M)	Sodium bicarbonate (10 ml; 10%)	Phenyl benzoate (**1b**)	25/RT	70	69	56
Glycine/0.01M	Benzoyl chloride (0.01M)	Sodium bicarbonate (10 ml; 10%)	Benzoyl glycine (**1c**)	33/RT	187**	185	63
Resorcinol/0.01M	Benzoyl chloride (0.01M)	Sodium bicarbonate (10 ml; 10%)	3-hydroxy phenyl benzoate (**1d**)	26/RT	135	131	86
Vanillin/0.01M	Benzoyl chloride (0.01M)	Sodium bicarbonate (10 ml; 10%)	4-Benzoyloxy-3-methoxy benzaldehyde (**1e**)	17/RT	77	74	57
1-Naphthol/0.01M	Benzoyl chloride (0.01M)	Sodium bicarbonate (15 ml; 10%)	Naphthalen-1-yl benzoate (**1f**)	48/RT	56	59	39
2-Naphthol/0.01M	Benzoyl chloride (0.01M)	Sodium bicarbonate (15 ml; 10%)	Naphthalen-2-yl benzoate (**1g**)	56/RT	107	105	43
4-Hydroxy acetanilide/ 0.01M	Benzoyl chloride (0.01M)	Sodium bicarbonate (10 ml; 10%)	4-Acetamido phenyl benzoate (**1h**)	09/RT	?	187	62
Salicylic acid/ 0.01M	Benzoyl chloride (0.01M)	Sodium bicarbonate (15 ml; 10%)	2-(Benzoyloxy) benzoic acid (**1i**)	38/RT	73**	76	09

*Slightly more; RT, Room temperature; R, Reported; F, Found; ?, Exact value unknown; **From website.

compounds including their synthetic transformation subsequently into amide (Ar′CONHAr/R) or ester derivatives (Ar′CO-OAr/R) in the presence of benzoylating agent in alkaline solvents (Schotten–Baumann reaction)[11–15]. Compared to acetylation (introduction of RCO-group) benzoylation is preferred due to superiority of benzoylated product/s, including their derivatives with respect to high melting point, aqueous insolubility, stability and resistance towards hydrolysis[16–18].

Chemically, inorganic or organic bases such as sodium hydroxide or pyridine are used extensively as primary catalysts providing the necessary alkaline liquid matrix sufficient to support benzoylation. Mechanistically, the high pH matrix helps in absorbing protons evolved during substitution and thus drifts the reaction forward along with enhancing the attacking power of the benzoylating agent. Whatever the alkaline matrix used for benzoylation is neither safe nor ecologically compatible and also difficult to recycle (Fischer scientific; msds; pyridine/sod hydroxide). On the other hand, when used for industrial purposes, they impose extensive financial burden in the manufacturing processes. However, the sodium bicarbonate matrix system being reported here is safe compared to classical alkaline solvents used industrially for benzoylation. In addition, we also tested one of our hypotheses – 'iceberg dancing of molecules' and found it to align with the results of this study.

The benzoylated derivatives were synthesized (under fuming hood) by dissolving or suspending equimolar quantity (0.01M) of reactants and benzoyl chloride (slightly more) in aqueous sodium bicarbonate matrix (10%; see Table 1 for details). The content was shaken for a sufficient period of time, yielding crude product which was further washed thoroughly with cold water initially followed by methanol (60%) and recrystallized from ethanol. The progression of reaction was monitored on pre-coated TLC plates (Merk) using PET ether : ethyl-acetate (8 : 2) as binary solvent system. The purity of reactants as well as synthesized products was evaluated in a UV chamber at 200–400 nm using planner chromatographic technique. Since physico-chemical and spectral characterization data of synthesized compounds are available, the same were further compared to enumerate synthetic practicability of sodium bicarbonate matrix in benzoylation.

The matrix for benzoylation was prepared by dissolving pre-desiccated sodium bicarbonate in distilled water. Qualitatively, pH of aqueous matrix was measured and compared with traditional solvents, which was found relatively less (8.7) despite it catalyses benzoylation of mono and polynuclear aromatic compounds smoothly and successfully (**1a**), though yield of some benzoylated derivatives was compromised (**1g–1i**). The aqueous sodium bicarbonate matrix reported here has been least studied, is non-carcinogenic and more advantageous compared to conventional alkaline analogs in ease of availability, non-hygroscopic characteristic, stability at a wide temperature range, noninflammable, non-volatile, economic, non-corrosive, eco-compatible, and devoid of toxic effects on the living population. (The method can be used in the laboratory to demonstrate benzoylation-related experiments to students in order to minimize their exposure to toxic chemicals.) Furthermore, benzoylation capacity of the same matrix was evaluated to protect the N-terminal end of amino acid (glycine). It was found that sodium bicarbonate matrix satisfactorily participates in benzoylation of glycine (**1c**); however, the net reaction time and yield had been compromised.

Among the synthesized compounds, **1a** (91%) was found in higher amounts followed by **1d** (86%), **1c** (63%), **1h** (62%), **1e** (57%), **1b** (56%), **1g** (43%) and **1i** (09%) in minute quantities. The extent of participation of sodium bicarbonate matrix in benzoylation of mono and polynuclear aromatic compounds was further established by calculating the reaction time ($R_T = R_2 - R_1$; where R_2 and R_1 indicate the time for completion and initiation of the reaction). The mononuclear ring system containing $–NH_2$ functionality benzoylated quickly and in higher yield (**1a**; 1 min 91%) than the mononuclear ring system containing –OH functionality (**1b**; 25 min 56%).

Anchimeric assistance of neighbouring functionalities on benzoylation efficiency of mononuclear ring/s containing –OH functionality in sodium bicarbonate matrix was also studied. It was found that the ring containing electron releasing group (ERG) as a secondary functionality participated in benzoylation easily; 'lesser the distance, higher the yield (**1d** > **1h**)', than ring systems containing electron withdrawing group (EWG); 'greater the inductive effect, lesser the yield (**1i** < **1e**)'. Furthermore, polynuclear unsubstituted ring bearing –OH functionality benzoylated last (**1f** > **1g**).

Structure-oriented study was also done to investigate rate of benzoylation in novel sodium bicarbonate matrix among ring systems containing –NH and –OH functionalities. It was found that monocyclic rings containing –OH/–NH functionality were easily benzoylated to a far greater extent than their polycyclic analogues owing to difference in distribution of electrons in single and multinuclear ring systems. However, rings containing –NH functionality react rapidly (1 min) giving higher yield (91% > 63% > 62%) of benzoylated derivatives (**1a** > **1c** > **1h**) than those containing –OH group due to greater electron releasing characteristic of amino functionality than that of hydroxyl functionality. Among mononuclear ring systems containing –OH group along with secondary functionalities, the one containing electron-releasing group benzoylated easily than rings systems containing electron withdrawing group due to assistance of electron releasing group in removing terminal proton of –OH and vice versa.

According to our results, aqueous sodium bicarbonate matrix could be used as an economic, safe and ecologically compatible solvent for large as well as small-scale benzoylation, especially for in-lab demonstration of experiments, preventing direct exposure of students to hazardous chemicals such as sodium hydroxide and/or pyridine, which are carcinogenic, corrosive, hygroscopic, difficult to handle, volatile, inflammable, and highly toxic in nature. Although overall yield of some benzoylated derivatives **(1f**, **1g** and **1i)** in sodium bicarbonate matrix is not comparable with classical solvents, synthetic portrait of this technique is unquestionable for **1a**, **1d**, **1h** and **1c** (may cause racemization according to previous study). The lower yield of some aforesaid benzoylated derivatives in aqueous sodium bicarbonate matrix could be enhanced either by employing substantially modified mixed solvent system containing certain minimum fixed percentage of conventional solvent along with bicarbonate matrix, or by enhancing the strength of aqueous matrix system used here.

Supporting information: Materials and methods with experimental procedure, including physio-chemical characteristics, qualitative analysis and spectral data of synthesized compounds is given in Supplementary Material.

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