

# Waste-Free Chemistry of Diazonium Salts and Benign Separation of Coupling Products in Solid Salt Reactions

Gerd Kaupp,\* Andreas Herrmann, and Jens Schmeyers<sup>[a]</sup>

**Abstract:** Gas–solid and solid–solid techniques allow for waste-free and quantitative syntheses in the chemistry of diazonium salts. Five techniques for diazotations with the reactive gases NO<sub>2</sub>, NO and NOCl are studied. Two types are mechanistically investigated with atomic force microscopy (AFM) and are interpreted on the basis of known crystal packings. The same principles apply to the cascade reactions that had been derived from one-step reactions. Solid diazonium salts couple quantitatively with solid diphenylamine and anilines to give the triazenes. Azo cou-

plings are achieved with quantitative yields by cautious co-grinding of solid diazonium salts with  $\beta$ -naphthol and C–H acidic heterocycles, such as barbituric acids or pyrazolinones. Solid diazonium salts may be more easily applied in a stoichiometric ratio for couplings in solution. Co-grinding of solid diazonium

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salts with KI gives quantitative yields of various solid aryl iodides. The unavoidable coupling products in salt reactions are completely separated from the insoluble products in a highly benign manner. The solid-state reactions compare favourably with similar solution reactions that produce much waste. The structures of the products are elucidated with IR and NMR spectroscopy and mass spectrometry, while the tautomeric properties of the compounds are studied with density functional calculations at the B3LYP/6–31G\* and BLYP/6–31G\*\* levels.

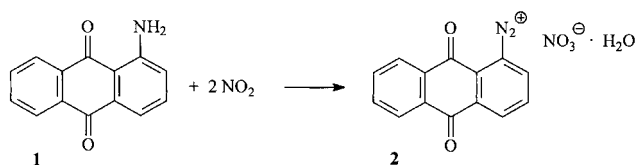
## Introduction

Solid diazonium nitrates are quantitatively obtained by the action of gaseous NO<sub>2</sub> on solid anilines.<sup>[1]</sup> These react quantitatively with dimethylamine to give triazenes.<sup>[1]</sup> We now explore further the solid-state syntheses of diazonium salts and solid-state couplings of these to anilines, diphenylamine,  $\beta$ -naphthol, barbituric acids, pyrazolinones and potassium iodide with quantitative yield. While most of these reactions may be performed in solution, only the solid-state reactions give quantitative yields and are thus highly superior by avoiding or minimizing waste. The solid-state mechanisms are studied in selected cases by atomic force microscopy (AFM).

## Results

**Solid-state diazotations:** Most versatile are diazotations of solid aromatic amines with NO<sub>2</sub> gas. The diazonium nitrate hydrates are quantitatively obtained. If the starting amine was not pure, the impurities could be removed after diazotation by washing with ethyl acetate.<sup>[1]</sup> A further application is the

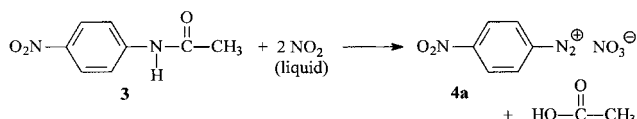
diazotation of 1-aminoanthraquinone (**1**) which gives quantitatively the monohydrate of the diazonium nitrate **2** (Scheme 1). Compound **2** was one of the first solid diazonium salts isolated.<sup>[2]</sup> It is rather insensitive to shock but explodes upon melting at  $\approx 126^\circ\text{C}$ .



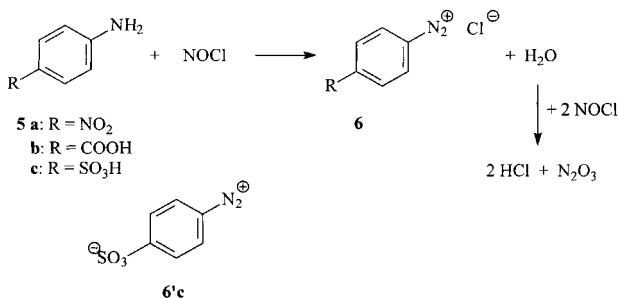
Scheme 1. Gas–solid synthesis of a stable diazonium nitrate hydrate by treatment with NO<sub>2</sub>.

A further synthetic approach is the conversion of acetanilides with NO<sub>2</sub>.<sup>[3, 4]</sup> It was found that the by-product acetic acid prevented the solid-state reaction as a result of passivation and (or) liquefaction. However, the use of liquid nitrogen dioxide at 5 °C is a preparatively useful pathway to solid anhydrous *p*-nitrophenyl diazonium nitrate (**4a**), which separates out quantitatively after evaporation of the excess of NO<sub>2</sub> and of the acetic acid. Unfortunately, solid phenyl and *p*-methyl-, *p*-chloro- or *p*-bromophenyl diazonium nitrates cannot be obtained in a pure form by this method because the diazotations are accompanied by nitrations of the aromatic rings in the starting aryl acetamides (Scheme 2).

[a] Prof. Dr. G. Kaupp, Dr. A. Herrmann, Dr. J. Schmeyers  
Universität Oldenburg  
FB Chemie, Organische Chemie I  
Postfach 2503, 26111 Oldenburg (Germany)  
Fax: (+49) 441-7983-409  
E-mail: kaupp@kaupp.chemie.uni-oldenburg.de

Scheme 2. Quantitative diazotation of an aryl acetamide with liquid  $\text{NO}_2$ .

Solid-state diazotations are not restricted to the synthesis of diazonium nitrates.<sup>[1]</sup> Solid anilines **5** can also be treated with gaseous  $\text{NOCl}$  to give solid diazonium chlorides **6** in 100% yield (Scheme 3). Thus, anhydrous **6a**, **6b** and the betaine **6'c** (after evaporation of  $\text{HCl}$ ) were obtained quantitatively as



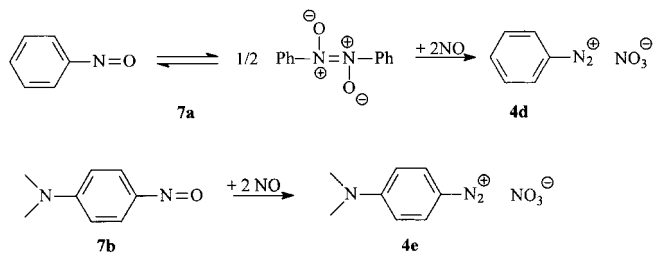
Scheme 3. Quantitative synthesis of aryl diazonium chloride hydrates or of a diazonium sulfonate.

judged by the weight increase and the  $^1\text{H}$  NMR spectra. The water produced by the reaction is removed by in situ reaction with excess  $\text{NOCl}$ . There is, therefore, a problem with the formation of a mixture of gases that cannot be reasonably separated for further use in small runs. However, the amount of waste formed by absorption of these gases in water and subsequent neutralisation is less severe than in non-quantitative solution diazotations, as only small quantities of inorganic sodium salts have to be disposed of, but not mixtures with

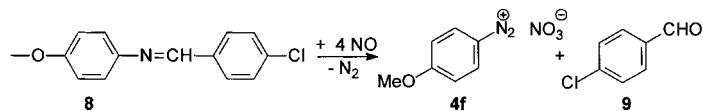
**Abstract in German:** Gas–Festkörper und Festkörper–Festkörper Techniken ermöglichen abfallfreie und quantitative Synthesen in der Diazoniumsalz-Chemie. Fünf Diazotierungs-Techniken werden untersucht, bei denen die Reaktivgase  $\text{NO}_2$ ,  $\text{NO}$  und  $\text{NOCl}$  zum Einsatz kommen. Zwei davon werden mittels Kraftmikroskopie (AFM) mechanistisch untersucht und auf der Grundlage bekannter Kristallpackungen gedeutet. Bei den Kaskaden-Reaktionen gelten offenbar dieselben Prinzipien wie sie aus einstufigen Reaktionen hergeleitet wurden. Feste Diazoniumsalze kuppeln quantitativ mit kristallinem Diphenylamin und festen Anilinen zu Triazenen. Azokupplungen gelingen mit quantitativer Ausbeute durch vorsichtiges Vermörsern fester Diazoniumsalze mit  $\beta$ -Naphthol und C–H-aciden Heterocyclen wie Barbitursäuren oder Pyrazolinonen. Feste Diazoniumsalze lassen sich auch leichter für stöchiometrische Azokupplungen in Lösung dosieren. Durch Vermörsern fester Diazoniumsalze mit  $\text{KI}$  entstehen zahlreiche feste Aryliodide mit quantitativer Ausbeute. Diese Reaktionen sind den Lösungsreaktionen derselben Typen vorzuziehen, bei denen viel Abfall entsteht. Die Konstitution der Produkte wird aus den IR-, NMR- und MS-Daten ermittelt. Die Tautomerie-Eigenschaften der Verbindungen werden auch mit Dichtefunktionaltheorie Rechnungen auf dem B3LYP/6–31G\* and BLYP/6–31G\*\* Niveau untersucht.

organic waste. No intermediate liquid phase occurred. However, the reactions were remarkably slow (one day) when compared with the diazotations with  $\text{NO}_2$ . It is difficult to obtain solid dry diazonium chlorides from solution reactions and even the yields in solution are as low as 10–50% if lots of corrosive waste is produced.<sup>[4]</sup>

Also Bamberger's method of obtaining diazonium salts from nitrosobenzenes **7a**, **b**<sup>[5]</sup> and nitrogen monoxide worked quantitatively in the solid state, whereas the yields of **4d** and **4e** in solution were as low as 70 and 49%, respectively (Scheme 4).<sup>[5, 6]</sup>

Scheme 4. Quantitative synthesis of diazonium nitrates from nitrosoaromatics and  $\text{NO}$ .

Even the synthesis of diazonium salts from aromatic imines (such as **8**) and nitrogen monoxide<sup>[7]</sup> can be performed in the solid state. The yields are better than in solution, although they are not quantitative and the aldehyde product must be extracted from the reaction mixture (Scheme 5).

Scheme 5. Diazonium salts from azomethine imines and  $\text{NO}$ .

We obtained the methoxy derivative **4f** in 80% yield as a solid after extraction of the 4-chlorobenzaldehyde (**9**) and 10% of a side product. In solution in diethyl ether,<sup>[7]</sup> a 65% yield of **4f** was obtained. As these interesting reactions may not be performed in a waste-free manner, they were not pursued in more detail.

**Mechanistic investigation by AFM:** The previous solid-state diazotations with gaseous  $\text{NO}_2$  had been studied with atomic force microscopy (AFM) to verify the three-step, solid-state mechanism (phase rebuilding, phase transformation, crystal disintegration).<sup>[1, 8, 9]</sup> It was of interest to discover whether the present multi-step reaction cascades would also exhibit long-range molecular movements and their correlation to the crystal structure. We chose the slow reaction of **5b** with  $\text{NOCl}$  and compared it with the more rapid, more involved reaction of **5b** with  $\text{NO}_2$ .<sup>[8]</sup>

Figure 1 presents the AFM results on the main face (001) of a single crystal of **5b** ( $P2_1/n$ )<sup>[10]</sup> in the reaction with  $\text{NOCl}$ , either diluted (1:5 with air) or undiluted, and which was applied by syringe from a distance of  $\approx 1$  cm (see the Experimental Section). The initial surface with molecular steps is rather flat (mean square roughness:  $R_{\text{ms}} = 0.73$  nm). After cautious application of diluted  $\text{NOCl}$ , very steep ( $> 45^\circ$ )

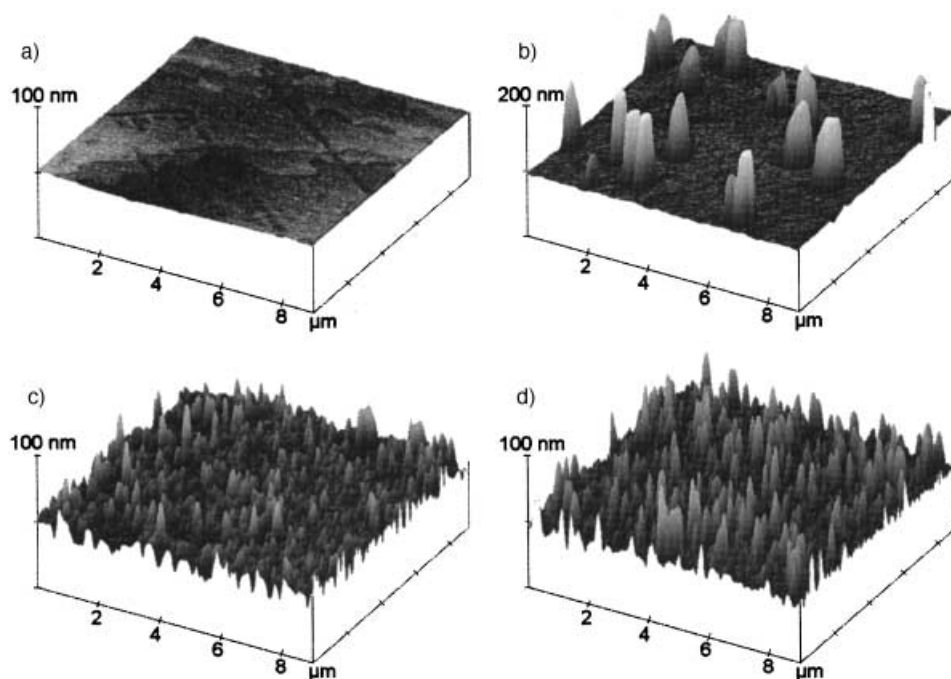


Figure 1. AFM topographies (9  $\mu\text{m}$ ) on (001) of **5b**: a) fresh; b) after application of 20% NOCl (2 mL); c) new sample after application of undiluted NOCl (5 mL); d) after application of undiluted NOCl (10 mL).

volcano-like islands formed (heights of 60–150 nm), while the low-level surface increased in roughness ( $R_{\text{ms}} \approx 1.8$  nm) by forming terrace-like flat covers (typical step height 2–6 nm). Interestingly, the appearance of the surface in Figure 1 b was very similar if 1 or 4 mL of diluted NOCl was applied. The amino groups are available at the surface and the molecules are sufficiently mobile, a fact that is proven by the random volcanoes visible upon reaction of **5b** with  $\text{NO}_2$ <sup>[8]</sup> and the

anisotropic formation of the islands here. However, passivation ensues probably due to some difficulties in the phase transformation that follows the phase rebuilding step.<sup>[8]</sup> Thus, the reaction stops under moderate conditions. That hindrance was partly overcome by more massive application of NOCl. The volcano features in Figure 1 c are almost randomly formed and much lower (heights up to 30 nm;  $R_{\text{ms}} = 5.3$  nm). Also the initial terraces seem to have undergone phase transformation as a result of a more violent reaction that helped to accelerate the process. In this case, the reaction continued upon further addition of reagent. The roughness increased from  $R_{\text{ms}} = 5.3$  nm to a value of 6.6 nm and the increased features (height up to

50 nm) are uniformly spread. Clearly, we have formation of rather large product crystallites and surface passivation that can be overcome.

The side face of **5b** (100) exhibits higher reactivity and shows a completely different behaviour. Large and wide hills are immediately formed with deep narrow valleys between them (Figure 2 b; maximum height 231 nm) that increased further (Figure 2 c; maximum height 256 nm) and disintegrated

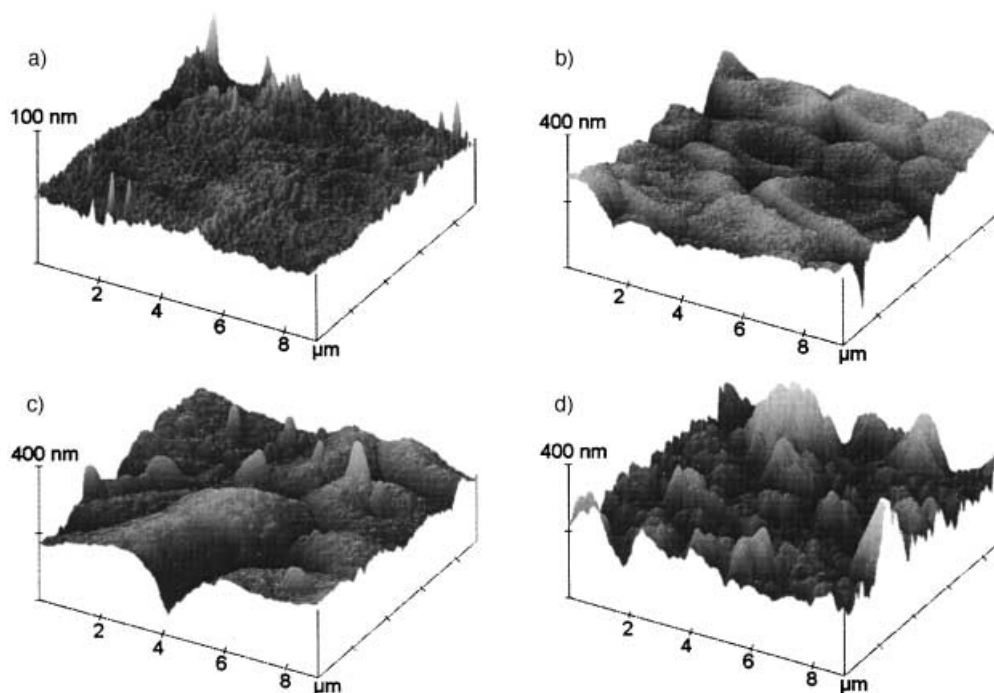
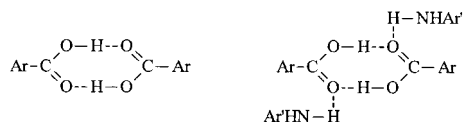


Figure 2. AFM topographies (9  $\mu\text{m}$ ) on (100) of **5b**: a) fresh; b) after application of 30% NOCl (2.5 mL); c) after application of 30% NOCl (10 mL); d) after application of 30% NOCl (20 mL).

ed to smaller features upon doubling the exposure (Figure 2d). The reason for this difference compared to Figure 1 lies in the crystal packing.

The lattice of **5b**<sup>[10]</sup> is very complicated. It exhibits hydrogen-bridged acid dimers (1.618 Å) without further bridging, as well as hydrogen-bridged dimers (1.710 Å) that form further hydrogen bonds to two amino groups (2.050 Å) (Scheme 6).



Scheme 6. Hydrogen bonding in the crystals of **5b**.

Furthermore, the molecules are aligned to form infinite ribbons. The packing diagram in Figure 3 shows the alignment of the molecules viewed along [010] in the form of a surface model. The independent ribbons that extend in the vertical direction are infinitely stacked and not interconnected. The shortest  $O \cdots H-N$  distance between neighbouring ribbons is 2.562 Å.

It is readily comprehensible that the main face (001) reacts more slowly than the lateral face (100), and that the reaction even halts under modest conditions. Exit of molecules over the (001) face upon reaction with NOCl is hindered by the infinite ribbons with their kinks. It requires a massive attack at high gas concentrations to overcome this handicap. On the other hand, attack of the gas on the long sides of the ribbons is virtually unimpeded and there is some direction of preference across the crystal parallel to the front plane in the [001] direction (Figure 2b). However, this is lost in the later stages of reaction. Furthermore, the uniformity of feature formation,

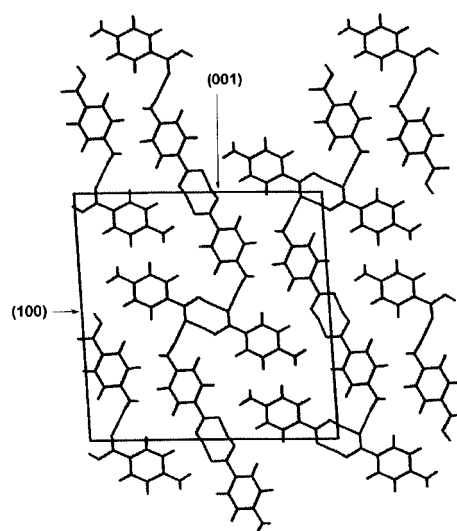


Figure 3. Packing diagram of a surface model of the crystal **5b** on (010) showing the projection of stacks of hydrogen-bonded ribbons that are quite flat and wind themselves down with kinks and are strongly interlocked because of the non-bridged “side groups”; the major natural faces extend towards the top/bottom and at the sides; hydrogen bonds are drawn.

shown in Figure 2b, c, is expected, as the outer amino groups are available everywhere. These observations are a clear-cut indication for the correlation of the solid-state reactivity and the crystal packing.

The reactions of NOCl with **5b** are slower than the reported reactions with  $NO_2$ .<sup>[8]</sup> Therefore, a comparison with the development of surface features in the latter reactions deserves consideration. Figures 4 and 5 show the course of the diazotations of **5b** with  $NO_2$  at a different stoichiometry to give the nitrate hydrate of **4b** (cf. **2**) on the (001) and (100) surfaces.

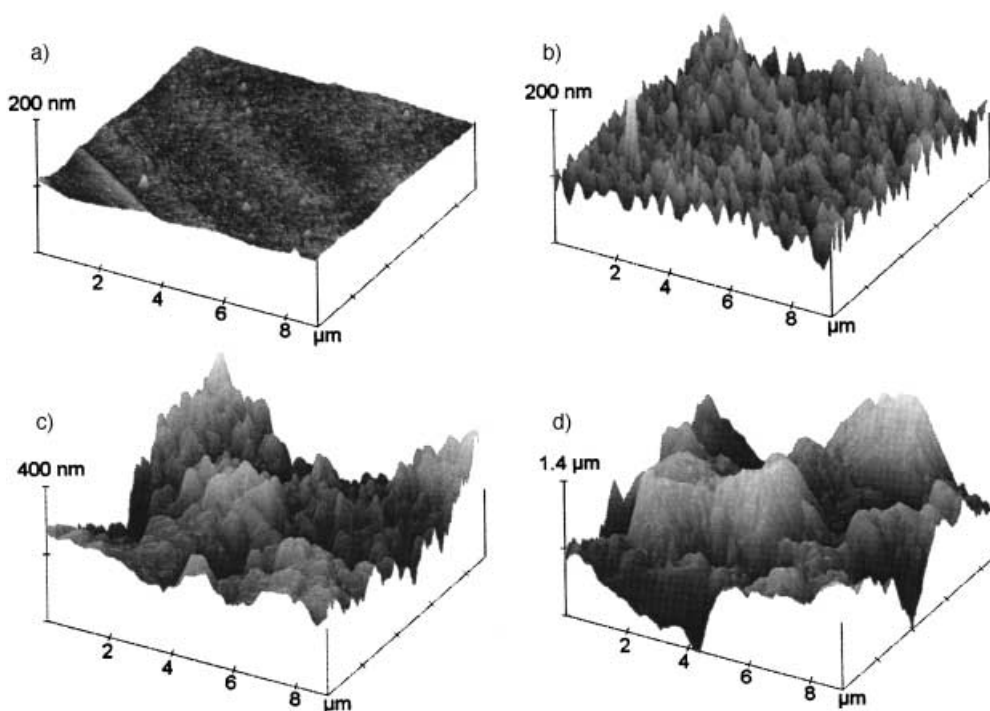


Figure 4. AFM topographies on (001) of **5b**; a) fresh; b) after application of 50%  $NO_2$  (1 mL); c) after application of 50%  $NO_2$  (2 mL); d) after application of 50%  $NO_2$  (4 mL).

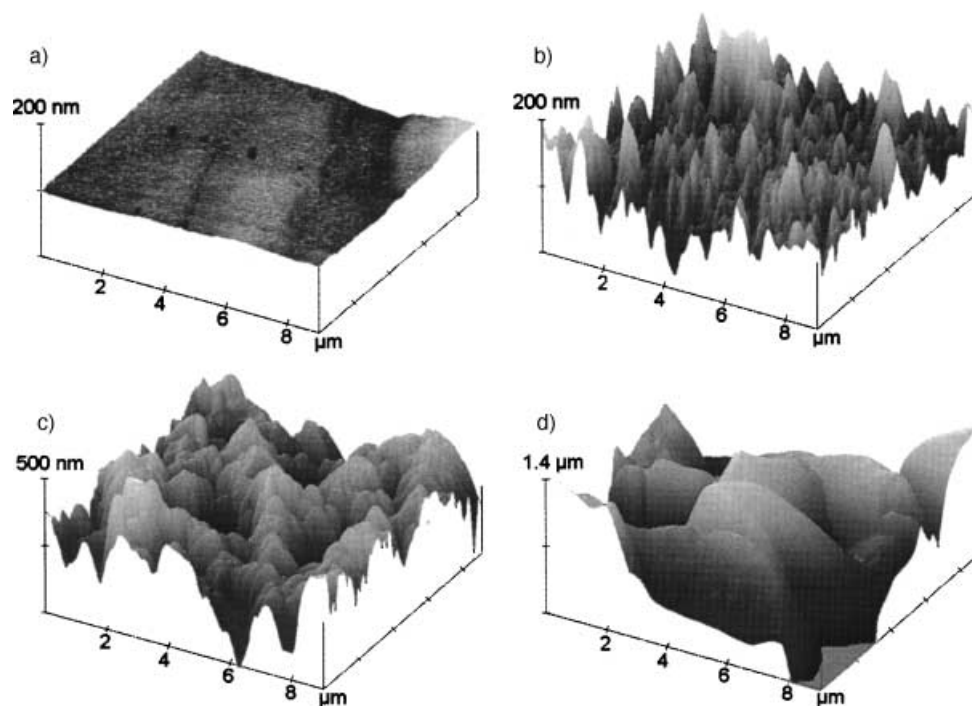


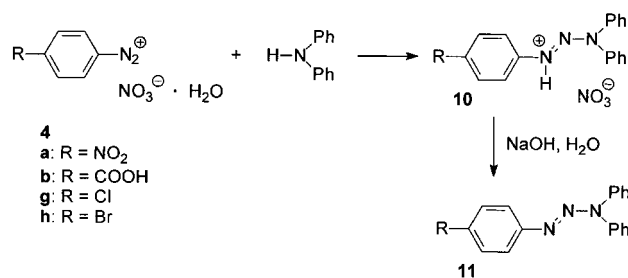
Figure 5. AFM topographies on (100) of **5b**; a) fresh; b) after application of 30%  $\text{NO}_2$  (0.1 mL); c) after application of 30%  $\text{NO}_2$  (0.2 mL); d) after application of 30%  $\text{NO}_2$  (0.5 mL).

Again, the (100) face is much more reactive than the (001) face of **5b**; however, unlike the results with  $\text{NOCl}$  there are no signs of passivation here. It appears that in the  $\text{NOCl}$  case, the system experiences some difficulties with phase transformation that are not present with  $\text{NO}_2$ . The lower tendency for crystallisation of the chloride **6b** as compared to the corresponding nitrate hydrate **4b** may be intuitively rationalised, although the starting conditions for attack and movements are the same for both reacting gases.

The AFM observations show again that reactivity problems can be tackled with AFM and that the suitability of the crystal structure (determining the phase rebuilding) for molecular movements upon reaction with the gas has to be complemented by a phase transformation capability. The same is true for the crystal disintegration step that is usually no problem, but may also impede solid-state reactions in rare cases.<sup>[11]</sup> It is important that the mechanistic principles that were derived from single-step reactions can also be applied to cascade reactions. These are of high synthetic interest on account of their high atom economy.

**Solid-state N-couplings with diphenylamine and anilines:** 1-Aryl-3,3-dialkyltriazenes are quantitatively prepared from solid diazonium salts and gaseous secondary amines.<sup>[11]</sup> As 1,1,3-triaryltriazenes can be obtained only with moderate yields in acidic, basic, or neutral solutions, it was of interest to try quantitative reactions of solid diazonium salts with solid diphenylamine (Scheme 7).

Careful grinding of diphenylamine with **4** gave quantitative yields of the nitrate salts **10**, from which the free triazenes **11** could be obtained by neutralisation (the stoichiometric coupling product  $\text{NaNO}_3$  is obtained in a pure form). The triazenes **11** exhibit characteristic  $\text{N}=\text{N}$  frequencies and



Scheme 7. Quantitative solid-state coupling with diphenylamine.

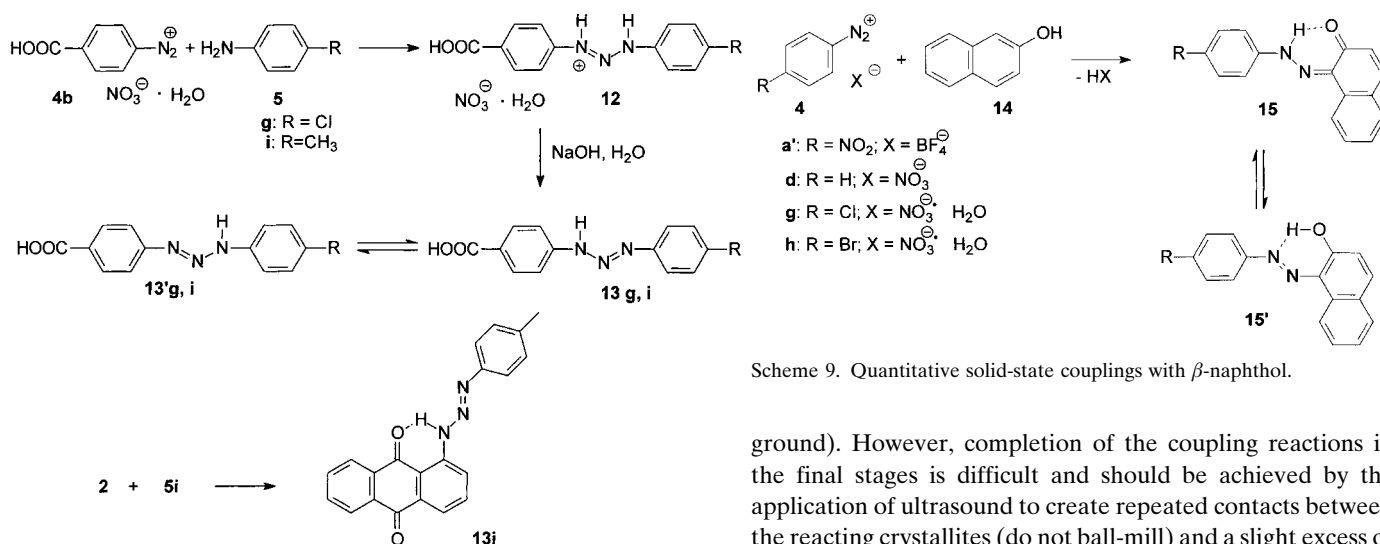
intense absorptions in their visible (Vis) spectrum (Table 1), as expected. The variations in the  $\text{N}=\text{N}$  vibration frequencies closely match those from density functional theory (DFT) calculations (BLYP; 6–31G\*\*\*) that predict a value of  $1386\text{ cm}^{-1}$  for **11b**. The  $\lambda_{\text{max}}$  values in the Vis spectra are similar to those reported in 95% ethanol;<sup>[12]</sup> however, we were also able to determine the  $\epsilon$  values in methanol which are remarkably large. The major fragment in the mass spectra of **11** is at  $m/z$  168 ( $\text{NPh}_2^+$ ). This facile access to 1,1,3-triaryltriazenes may be useful for their application as cytotoxic reagents.<sup>[13]</sup>

The success in the synthesis of triaryltriazenes prompted us to make use of the advantages of solid-state reactions in the syntheses of 1,3-diaryl-triazenes, which are known to cleave in acidic solution, rearrange (transdiazotation and formation of aminoazo compounds) and tautomerise.<sup>[4]</sup> It was hoped that side reactions could be avoided in the solid state and indeed, there was no trouble in obtaining quantitative yields of the salts **12** and the free triazenes **13** by co-grinding and neutralisation (Table 1) (the stoichiometric coupling product  $\text{NaNO}_3$  is obtained in a pure form; Scheme 8).

Table 1. Yields and characteristic IR and Vis data of 1-aryl-3,3-diphenyltriazenes **11** and 1,3-diaryltriazenes **13**.

<b>11</b> or <b>13</b>	R	Reaction time [h]	Yield solid state [%]	Yield in solution [%]	$\tilde{\nu}_{\text{N=N}}$ KBr [cm <sup>-1</sup> ]	$\nu_{\text{N=N}}$ [cm <sup>-1</sup> ] <sup>[14]</sup>	$\lambda_{\text{max}}$ MeOH [nm]	$\epsilon$ [L mol <sup>-1</sup> cm <sup>-1</sup> ]	$\lambda_{\text{max}}$ (95 % EtOH) [nm]
<b>11a</b>	NO <sub>2</sub>	3	> 99	60 <sup>[14]</sup>	1384	1395	431	19 500	449 <sup>[12]</sup>
<b>11b</b>	COOH	6	> 99	69 <sup>[14]</sup>	1385	1393	423	20 400	439 <sup>[12]</sup>
<b>11g</b>	Cl	3.5	> 99	64 <sup>[14]</sup>	1383	1394	416	20 400	411 <sup>[12]</sup>
<b>11h</b>	Br	3	> 99	72 <sup>[14]</sup>	1418	1404	419	20 400	411 <sup>[12]</sup>
<b>13g</b>	Cl	24	> 99		1386		360	26 300	360 <sup>[15]</sup>
<b>13i</b>	CH <sub>3</sub>	24	> 99		1385		359	24 500	359 <sup>[15]</sup>
<b>13j</b>	Anq <sup>[a]</sup>	12	> 99	89 <sup>[16]</sup>	1353, 1407		470 <sup>[b]</sup>	10 500 <sup>[b]</sup>	

[a] Anq = 2,3-(C=O)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>. [b] Also 368/22 400 [16].



Scheme 8. Quantitative solid-state syntheses of tautomeric triazenes.

The tautomerism of **13** was judged by DFT calculations in terms of energy content (B3LYP/6–31G\*) and N=N vibration (BLYP/6–31G\*\*). Compound **13g** is more stable than **13'g** by 1.2 kcal mol<sup>-1</sup> and the N=N vibrational frequency (1386 cm<sup>-1</sup>) agrees with the calculated value of **13g** (1383 cm<sup>-1</sup>), but not with **13'g** (1356 cm<sup>-1</sup>). Similarly, the most stable tautomer of **13j** is calculated to exhibit an energetic preference of 9.3 kcal mol<sup>-1</sup> over its best 1,3-H-shifted tautomer as well as a single minimum intramolecular hydrogen bond (N–H: 1.025 Å; O...H: 1.849 Å). The long-wavelength UV maxima of **13g–i** are ≈ 60 nm shorter than those of **11** (Table 1). This again seems to favour **13** and not **13'**. Further studies and applications of these triazenes will now be facilitated by the ease of their accessibility.

**Solid-state azo coupling with β-naphthol and C–H acidic heterocycles:** The solid-state azo coupling of 4-bromobenzenediazonium nitrate hydrate (**4h**) with β-naphthol was studied by AFM.<sup>[11]</sup> Far-reaching movements of β-naphthol molecules across the contact sites into the diazonium salt crystals were detected. These movements could be correlated to the crystal structure of β-naphthol (**14**). Such coupling is preparatively useful and gives the “azo dyes” **15** in quantitative yield (Scheme 9). As ball-milling should not be used for safety reasons, the initially violent reactions have to be started cautiously by grinding and mixing (**4a'** and **14** may be co-

Scheme 9. Quantitative solid-state couplings with β-naphthol.

ground). However, completion of the coupling reactions in the final stages is difficult and should be achieved by the application of ultrasound to create repeated contacts between the reacting crystallites (do not ball-mill) and a slight excess of **14** to give **15** in quantitative yields and in reasonable times. Such an excess and the salts NaNO<sub>3</sub> or NaBF<sub>4</sub> have to be removed with aqueous NaOH; some waste (**14**) is produced in addition to a simple salt. However, we have quantitative yields whereas further auxiliaries are needed in the corresponding solution reactions that produce side reactions.<sup>[17]</sup> Therefore, it is not surprising that no yields were reported for **15** (or the other compounds of Table 2) in the primary literature.

Internal hydrogen bonding and tautomerisation of “azo-naphthols”, such as **15/15'**, in the crystalline state have been studied by IR spectroscopy.<sup>[18]</sup> X-ray structural analysis<sup>[19, 20]</sup> and <sup>13</sup>C NMR spectroscopy<sup>[20]</sup> confirmed the structures **15a, d**. Further support is provided by the values of the C=O and C=N vibrations predicted with DFT calculations at the BLYP/6–31G\*\* level, which correspond reasonably well with the experimental values. Our DFT calculations at the B3LYP/6–31G\* level predict that the hydrazone structures **15a, d, g** are more stable than the azo structures **15'a, d, g**, by 3.6, 2.8 and 2.6 kcal mol<sup>-1</sup>, respectively. Thus, the preference of these “azo dyes” for tautomer **15** seems to be inherent to the isolated molecules.

It is well-known that the *p*-dimethylamino derivative **15'** (R = NMe<sub>2</sub>)<sup>[20]</sup> assumes an azo structure in the crystalline state. B3LYP/6–31G\* calculations predict that this azo tautomer is 1.2 kcal mol<sup>-1</sup> less stable than its hydrazone tautomer **15** (R = NMe<sub>2</sub>); however, there is an additional hydrogen-bond acceptor in these molecules that makes it difficult to judge the differences in the energies of crystallisation from these results.

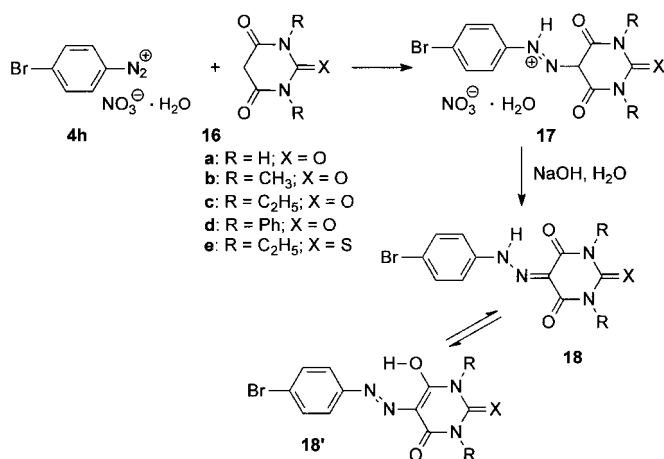
Table 2. Solid-state C-coupling of diazonium salts and yields.

Dye	R	Reaction time [h]	Yield solid-state reaction [%]	Comment	Yield solid to solution reaction [%]
<b>15a</b>	NO <sub>2</sub>	48 <sup>[a]</sup>	100	1.2 <b>14</b> ; <b>4a'</b> : 97%	92
<b>15d</b>	H	48 <sup>[a]</sup>	100	1.2 <b>14</b>	
<b>15g</b>	Cl	48 <sup>[a]</sup>	> 99	1.2 <b>14</b>	
<b>15h</b>	Br	12 <sup>[b]</sup>	> 99	1.2 <b>14</b> ; 1 MgSO <sub>4</sub>	
<b>18a</b>	H	24 <sup>[b]</sup>	100		100
<b>18b</b>	CH <sub>3</sub>	24 <sup>[b]</sup>	> 99		
<b>18c</b>	C <sub>2</sub> H <sub>5</sub>	24 <sup>[b]</sup>	> 99		
<b>18d</b>	Ph	24 <sup>[b]</sup>	> 99		
<b>18e</b>	C <sub>2</sub> H <sub>5</sub>	24 <sup>[b]</sup>	> 99		
<b>21a</b>	NO <sub>2</sub>	12	> 98	(CH <sub>3</sub> ) <sub>3</sub> N <sup>[c]</sup>	95 <sup>[d]</sup>
<b>21f</b>	CH <sub>3</sub> O	12	> 99	(CH <sub>3</sub> ) <sub>3</sub> N <sup>[c]</sup>	
<b>21h</b>	Br	12	> 98	(CH <sub>3</sub> ) <sub>3</sub> N <sup>[c]</sup>	

[a] The last 24 h under ultrasound exposure. [b] After the co-grinding under ultrasound exposure. [c] Reaction accelerated at its final stage by exposure to (CH<sub>3</sub>)<sub>3</sub>N. [d] 92% pure; 81% after crystallization.

The technical complications in the couplings of **4** with **14** prevented us from tackling the problem of intermediate diazoethers<sup>[4]</sup> that was put forward by Tezuka et al.,<sup>[21]</sup> who showed their absence in “normal” azo couplings.

C couplings of solid diazonium salts are not restricted to phenols. Co-grinding and ultrasound exposure with barbituric acid (derivatives) gives quantitative yields of tautomeric<sup>[22]</sup> “5-arylo barbituric acids”. The formation of the salts **17** is waste-free, but if quantitative yields of the neutral compounds **18** are required, then the neutralisation with NaOH forms the salt NaNO<sub>3</sub> as an unavoidable stoichiometric coupling product. The neutralisation process is highly benign, at least in comparison with neutralisations of acid solutions (large excess) containing organic waste from solution diazotations followed by coupling reactions. Only the NaNO<sub>3</sub> from the solid-state reactions is highly pure. Even more importantly, the compounds **18** do not require purification when synthesised in the solid state (Scheme 10). The chemical structures of



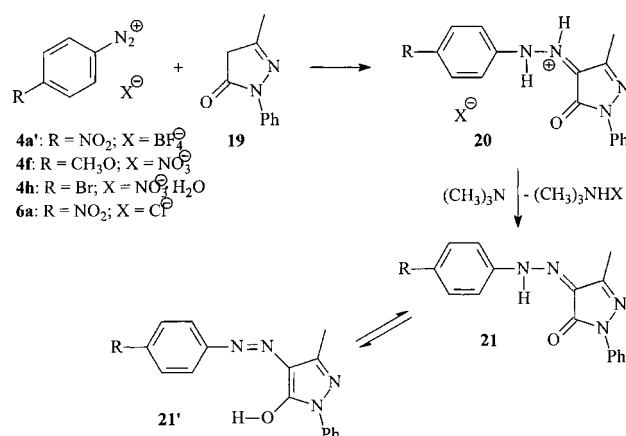
Scheme 10. Quantitative solid-state couplings with barbituric acids.

the compounds were secured by comparison with the known compound **18a**,<sup>[23]</sup> their IR, UV/Vis, and NMR spectra, their fragmentation in the MS, and their HRMS data. The azo/

hydrazone tautomerism of **18** may depend on the state (gas, solid, solution) and the temperature. Density functional B3LYP calculations (6–31G\*) predict that the hydrazone tautomer **18** is considerably more stable than the azo tautomer **18'**. The energy differences are 13.7 or 13.2 kcal mol<sup>-1</sup> for the models **18a/18'a** in which the Br is replaced by H or Cl (an azo structure with sp<sup>3</sup> carbon would be even worse: 21.5 kcal; Br replaced by H). It appears unlikely that the crystals of **18** could favour the tautomers **18'** in view of those large differences of the undoubtedly intramolecularly hydrogen-bridged structures.

The IR frequencies in the range of  $\nu = 1400\text{--}1515\text{ cm}^{-1}$  (three characteristic vibrations around 1513, 1436, 1406) have been termed characteristic for the azo structure **18'**.<sup>[23]</sup> These are present in the solid-state IR spectra of all five compounds **18 a–e**. However, we do not interpret these as belonging to **18'**. Rather, our DFT calculations for the estimation of the vibration frequencies (BLYP/6–31G\*\*) do not find a minimum for **18'** (Br replaced by H) but convert such a structure into the hydrazone tautomer **18**.

The azo-coupling products of 3-methyl-1-phenyl-2-pyrazolin-5-one (**19**) with **4** have been formulated with the hydrazone structure **21** (Scheme 11).<sup>[24, 25]</sup> Even these coupling products were obtained quantitatively in the solid state;



Scheme 11. Quantitative solid-state couplings with a pyrazolinone.

however, the reactions are rather slow and should therefore be completed by the action of gaseous trimethylamine on the pre-reacted co-ground mixture. Apparently, the acid–base reaction with salt formation creates ample new contacts between the reacting crystals of **4** and **19**. The base may also increase the reactivity of **19**. In solution, the isolated yield of **21a** was 81% (Table 2). The products **21**<sup>[24, 25]</sup> are characterised by their m.p., IR and NMR spectra.

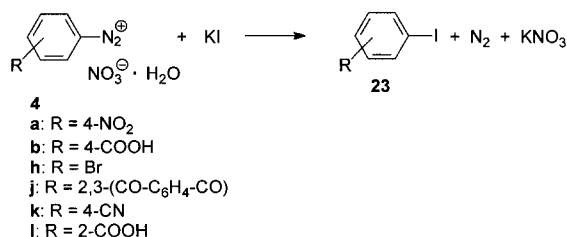
The hydrazone structure of **21** is secured by density functional calculations at the B3LYP/6–31G\* level which predict that the azo tautomer (for the model **21/21'** with R = H) is 10.7 kcal mol<sup>-1</sup> higher in energy.

In solution, the <sup>1</sup>H NMR signal of the NH group at  $\delta = 13.5\text{--}13.8$  for **21a, f, h** indicates strong chelation. Finally, an X-ray structure analysis<sup>[26]</sup> provided compelling evidence for the hydrazone structure **21a**.

As the solid-state coupling reactions with **14** and **19** are not free of some organic waste (recycling does not appear to be

worthwhile in these lab-scale experiments), one may also consider performing these reactions in solution according to standard procedures,<sup>[17]</sup> but with the application of solid diazonium salts instead of highly acidic diazotation solutions. The 80% yield of parared **15a**, which is described in a standard textbook used in German Universities,<sup>[17]</sup> is hardly attainable by the described technique; however, the yield increased to 92% by the addition of one equivalent of solid **4a'** to the basic solution of **14** and not by the use of HCl (see Experimental Section). A similar technique was attempted in the synthesis of **18a**: a stoichiometric amount of solid **4h** was added to a buffered (NaOAc) slurry of **16a** in aqueous ethanol, and the yield was quantitative. In the case of **21a**, a 95% raw yield (92% purity; 81% yield after recrystallisation) was obtained in EtOH/H<sub>2</sub>O/NaOAc when a stoichiometric quantity of solid **4a** was used. Clearly, the solid-state couplings are superior in all respects both to the application of a solid to dissolved coupling component and more so to the common standard techniques, despite some of their technical problems (no ball-milling of solid diazonium salts) that are not present in numerous other solid-state syntheses.<sup>[11]</sup>

**Solid-state aromatic iodination:** Little is known about the use of inorganic halide salts for organic solid-state substitution reactions. The high reactivity of solid diazonium salts prompted their co-grinding with KI and indeed, quantitative yields of solid aryl iodides **23** were obtained in the solid state (IR control) as shown in Scheme 12. Clearly, such favourable



Scheme 12. Quantitative solid-state iodination of diazonium salts.

behaviour would also be interesting for radio-iodide derivatives that might be used in metabolism studies.<sup>[27, 28]</sup> These syntheses are particularly versatile. Unlike the corresponding solution reactions (reported yields range from 60% to 90%,<sup>[17]</sup> “nearly quantitative”, or unspecified) that produce iodine,<sup>[29]</sup> phenols and side products via aryl radicals (the products separate out during reaction),<sup>[4]</sup> the solid-state syntheses are clean, all give 100% yield (**4k** and **4l** are described in reference [1]) and no organic waste is formed. We did not find traces of iodine or biaryls in the careful mass-spectrometric analyses. Thus, we conclude that the solid-state process is purely ionic in character. The grinding process takes 5 min, though several portions may be ground for 5 min each in excess KI. For completion of the reactions, the mixture was allowed to stand for 24 h with occasional grinding. We have not yet been able to decide if a possible water layer on the KI crystals may play a significant role in these reactions. It could be shown that freshly ball-milled KI (15 min; 514.4 mg) did not gain in weight when spread on a watch glass and left in an

ambient atmosphere at 22–25 °C at a relative humidity of 50–60% for three days, and it kept its appearance under a microscope at 400-fold magnification.

Numerous solid aryl iodides might be accessible in quantitative yield from further solid anilines. Our tested diazonium salts did not give aryl bromides or chlorides when KBr or NaCl pellets were prepared for IR spectra. However, it can be envisaged that appropriate catalysts might facilitate solid-state Sandmeyer reactions with KBr or KCl to afford aryl bromides and chlorides.

## Discussion

Waste-free solid-state diazotations and reactions of solid diazonium salts are versatile, despite their cascade character and varied reaction types. They can be safely executed when all measures of precaution are taken into account. Numerous open questions in diazonium salt chemistry can now be easily revisited.

The solid-state formation of diazonium salts is clearly evidenced by the AFM studies (Figures 1, 2, 4 and 5) that correlate with the crystal structure of the starting crystal of **5b**, despite the multiple cascades in the different diazotation reactions. Furthermore, they give convincing explanations for the differences in reactivity on different faces and with different reacting gases (NOCl and the radical NO<sub>2</sub>).

Various triazenes can now be readily synthesised and spectroscopically characterised and their tautomerism can be assessed. Even C couplings with  $\beta$ -naphthol and C–H acidic coupling reagents could be safely brought to completion with extreme care in the synthesis of **15** because of the very high reactivity, and less violently in the syntheses of **18** and **21**. Only the latter required an auxiliary reagent for rapid completion. The “azo dyes” formed quantitatively owing to the optimum selectivity in the solid-state reactions. However, apparently all of them prefer their hydrazono tautomer either as isolated molecules, according to B3LYP/6–31G\* density functional calculations, or as solids, according to IR and X-ray structural evidence. The previous assignment of the azo form **18**<sup>[23]</sup> cannot be maintained in view of the distinct B3LYP/6–31G\* results that favour **18**.

It is noticeable that even the ionic crystals of KI could be used for the quantitative synthesis of solid aryl iodides **23** in solid-state reactions by co-grinding with solid diazonium salts. There was no liquid phase, and freshly ball-milled KI is not hygroscopic. Many of the presented reactions are waste-free and the pleasant implications are discussed in detail in this paper. Of course, there are also limitations that we mention and some difficulties that arise from the fact that solid diazonium salts must not profit from the benefits of ball-milling for safety reasons. If neutral products are formed from salts, then coupled product salts are always produced. The benign strategy ensures that safe and neutral inorganic salts can be extracted with water in pure form and only in stoichiometric quantities, as opposed to undue amounts of salts from salting out techniques and from the neutralisation of concentrated acids that may arise from low-yield diazotations with couplings and which additionally contain organic



waste matter. The highest benefit of the quantitative solid-state reactions is the avoidance of waste-producing purification steps since the products arise directly in the pure state.

## Experimental Section

**Caution:** Solid diazonium salts explode upon heating to their melting point and they are shock sensitive (hammer and anvil test). Thus, precautions should be taken when handling them. All reactions described herein tend to be exothermic and must be slowed down in order to remove the heat efficiently. Solid diazonium salts must not be ground in mortars with sharp edges but only cautiously in agate mortars and pestles with smooth surfaces. We never used ball mills to grind solid diazonium salts in order to avoid any risk of explosion. No risks were experienced if the experimental conditions in this work were strictly followed. For violently reacting crystal mixtures, the single components should be separately ground, then carefully mixed, left to react and finally treated with ultrasound (common cleaning bath at 20–25 °C) to complete the reaction.

The product yields were detected by weight; the reaction success was monitored by IR spectroscopy in KBr. After disappearance of the diazonium band, at least 10% of the reaction time was additionally used to secure completion of the process. The purity of the products was secured by m.p., thin-layer chromatography and <sup>1</sup>H NMR spectroscopy.

The experimental error in the determination of the yields was judged to be ±1%. The solid-state<sup>[1,8]</sup> and AFM techniques<sup>[11]</sup> have been described in detail elsewhere. Surface scraping was avoided<sup>[11, 30, 31]</sup> and all supermicroscopic images were stable for at least 10 scans. Single crystals of **5b** were obtained from ethanol by slow evaporation. Gases were applied to the mounted single crystal by syringe from a distance of ≈1 cm under a hood. After 1 min exposure time, the gas was flushed away with a stream of air. Vacuum tightness is essential in preparative gas–solid reactions, leakages must be sealed prior to the reaction. The NMR spectra (<sup>13</sup>C in bb mode) were recorded with a Bruker WP300, UV/Vis spectra with a Perkin-Elmer Lambda 551 S spectrometer, FT-IR spectra with a Perkin-Elmer 1720-X (not all frequencies are reported) and mass spectra with a Finnigan MAT212 instrument. For common compounds, spectral data were restricted to data not previously available.

B3LYP (basis set 6–31G\*) and BLYP (basis set 6–31G\*\*) calculations with full geometry optimisation were performed with the program TITAN, version 1.01, of Wavefunction, Inc., Irvine (USA).

**1-(9,10-Anthraquinone)diazonium nitrate hydrate (2):** Compound **1** (690 mg, Aldrich, 97% purity, 3.00 mmol) was evacuated in a 250 mL flask and then exposed to NO<sub>2</sub> (360 mg, 7.8 mmol) at 0.7 bar for 3 h at room temperature with occasional shaking. The excess gas was condensed into a trap at 77 K, and the solid was washed with ethyl acetate (2 × 10 mL) to remove the nonpolar impurities (not necessary if a pure starting material is used). Yield of **2**·H<sub>2</sub>O: 940 mg (100%); m.p. 126 °C (exploded) (ref. [2]: 120 °C); IR (KBr):  $\bar{\nu}$  = 2290 (N<sub>2</sub><sup>+</sup>), 1685 (C=O), 1590, 1385, 1329, 1290, 1174, 1133, 1069, 705 cm<sup>-1</sup>; <sup>1</sup>H NMR (CF<sub>3</sub>COOD):  $\delta$  = 9.52 ( $\psi$ d, abc, 1H), 9.42 ( $\psi$ d, bac, 1H), 8.88–8.72 (m, 3H), 8.46–8.34 (m, 2H); <sup>13</sup>C NMR (CF<sub>3</sub>COOD):  $\delta$  = 182.13, 180.96, 142.45, 142.18, 139.65, 138.92, 138.73, 138.41 (C<sub>quat</sub>), 136.14 (C<sub>quat</sub>), 134.42 (C<sub>quat</sub>), 133.60 (C<sub>quat</sub>), 130.95 (2C), 114.43 (C<sub>quat</sub>).

**Diazotation of 3 with liquid nitrogen dioxide:** Compound **3** (360 mg, 2.00 mmol) was cooled to 5 °C. NO<sub>2</sub> (≈1 g) was condensed in a vacuum line onto the crystals that slowly dissolved overnight at 5 °C in a refrigerator. Excess NO<sub>2</sub> was recovered at 10 °C by condensing into a cold trap at 77 K for further use. The acetic acid was removed in a vacuum at 25 °C (it might be used or neutralised with NaOH). The quantitatively obtained diazonium nitrate **4a** (212 mg, 100%) was characterised by its IR and NMR spectra.<sup>[1]</sup>

**Solid-state diazotations with nitrosyl chloride:** The solid anilines **5a–c** (1.00 mmol) in a 250 mL flask were connected by a vacuum line to a 250 mL flask that was filled with NOCl (1 bar, 11 mmol). After one day, the gases were condensed back into the gas reservoir at 77 K, absorbed in water and neutralised with NaOH for disposal. The yellow-orange crystals were weighed and analyzed.

**4-Nitrobenzenediazonium chloride (6a):** Yield 184 mg (100%); m.p. 120 °C (exploded); IR (KBr):  $\bar{\nu}$  = 2283 (N<sub>2</sub><sup>+</sup>), 1609, 1537 (NO<sub>2</sub>), 1388, 1316 (NO<sub>2</sub>) cm<sup>-1</sup>; <sup>1</sup>H NMR (CF<sub>3</sub>COOD):  $\delta$  = 9.00 (AA'BB', 2H), 8.82 (BB'AA', 2H); <sup>13</sup>C NMR (CF<sub>3</sub>COOD):  $\delta$  = 156.71 (C<sub>quat</sub>), 136.33 (2C), 128.89 (2C), 121.89 (C<sub>quat</sub>).

**4-Carboxybenzenediazonium chloride (6b):** Yield 183 mg (100%); m.p. 119 °C (exploded); IR (KBr):  $\bar{\nu}$  = 2553, 2455, 2304 (N<sub>2</sub><sup>+</sup>), 1710 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CF<sub>3</sub>COOD):  $\delta$  = 8.82 (AA'BB', 2H), 8.72 (BB'AA', 2H); <sup>13</sup>C NMR (D<sub>2</sub>O):  $\delta$  = 166.65, 141.67 (C<sub>quat</sub>), 132.71 (2C), 132.38 (2C), 118.49 (C<sub>quat</sub>).

**4-Benzenediazoniumsulfonate (6c):** Yield: 183 mg (100%); m.p. 104 °C (exploded); IR (KBr):  $\bar{\nu}$  = 2304 (N<sub>2</sub><sup>+</sup>), 1659, 1635, 1574, 1409, 1385, 1244, 1212 cm<sup>-1</sup>; <sup>1</sup>H NMR (D<sub>2</sub>O):  $\delta$  = 8.57 (AA'BB', 2H), 8.09 (BB'AA', 2H); <sup>13</sup>C NMR (D<sub>2</sub>O):  $\delta$  = 154.47 (C<sub>quat</sub>), 133.59 (2C), 129.13 (2C), 115.75 (C<sub>quat</sub>).

**Diazotation of solid nitrosobenzene (7a) to give 4d:** Compound **7a** (214 mg, 2.00 mmol) was evaporated in a 250 mL flask and then connected by a vacuum line to a 250 mL flask containing NO (≈1 bar, 11 mmol) that had been freed from traces of NO<sub>2</sub> by storing over 4-chloroaniline (1 g) for 24 h (the partly diazotised 4-chloroaniline gives a 100% yield of **4g** if NO<sub>2</sub> is applied afterwards). After the sample had been kept in a refrigerator at 4 °C for 24 h, excess gas was recovered in a cold trap. Pure **4d** (333 mg, 100%) was obtained; m.p. 87 °C (exploded); the purity was checked by quantitative solid-state coupling with  $\beta$ -naphthol to give **15d** (see below); IR (KBr):  $\bar{\nu}$  = 2293 (N<sub>2</sub><sup>+</sup>), 1569, 1485, 1461, 1385 (NO<sub>3</sub><sup>-</sup>) cm<sup>-1</sup>; <sup>1</sup>H NMR: decomposition in D<sub>2</sub>O and CF<sub>3</sub>COOD.

**Diazotation of solid 4-dimethylaminonitrosobenzene (7b) to give 4e:** Compound **7b** (300 mg, Aldrich, 97% purity, 1.94 mmol) was evaporated in a 250 mL flask and then connected by a vacuum line to a 250 mL flask containing NO (≈1 bar, 11 mmol) that had been freed from traces of NO<sub>2</sub> by storing over 4-chloroaniline (1 g) for 24 h. After storing the sample in a refrigerator at 4 °C for 48 h, excess gas was recovered in a cold trap at 77 K. The sample was washed with dry ether to remove non-polar impurities. Spectroscopically pure **4e** (407 mg, 100%) was obtained; m.p. 127 °C (exploded) (ref. [6]: 128 °C); IR (KBr):  $\bar{\nu}$  = 2151 (N<sub>2</sub><sup>+</sup>), 1594, 1538, 1390 (NO<sub>3</sub><sup>-</sup>) cm<sup>-1</sup>; <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 8.12 (AA'BB', 2H), 6.98 (BB'AA', 2H), 3.25 (s, 6H).

**Diazotation of solid (4-chloro)benzylidene-(4-methoxy)aniline (8) to give 4f:** Compound **7** (491 mg, 2.00 mmol) was evaporated in a 250 mL flask and then connected by a vacuum line to a 250 mL flask containing NO (≈1 bar, 11 mmol) that had been freed from traces of NO<sub>2</sub> by storing over 4-chloroaniline (1 g) for 24 h. After 24 h, excess gas was recovered in a cold trap and the solid material washed with dry ether (2 × 10 mL). Spectroscopically pure **4f** (315 mg, 1.60 mmol, 80%) was obtained; m.p. 126 °C (exploded) (ref. [7]: 129 °C, decomp); IR (KBr):  $\bar{\nu}$  = 2249 (N<sub>2</sub><sup>+</sup>) cm<sup>-1</sup>; <sup>1</sup>H NMR (CF<sub>3</sub>COOD):  $\delta$  = 8.32 (AA'BB', 2H), 7.29 (BB'AA', 2H), 4.02 (s, 3H); <sup>13</sup>C NMR (CF<sub>3</sub>COOD):  $\delta$  = 173.98 (C<sub>quat</sub>), 137.41 (2C), 120.36 (2C), 101.42 (C<sub>quat</sub>), 58.92.

**1-Aryl-3,3-diphenyltriazenes 11 and 1,3-diaryltriazene 13:** Diphenylamine or substituted anilines (1.00 mmol) were ground in an agate mortar. Then the diazonium nitrate hydrate **4** (1.00 mmol) was added in five portions and co-ground for 5 min. To complete the reaction, the solid mixture was transferred to a test tube and then exposed to ultrasound in a cleaning bath, the temperature of which was maintained at 20–25 °C, for 3–6 h or 24 h until all of the diazonium band in the IR had disappeared. The solid was triturated with 0.1N NaOH (20 mL), filtered, thoroughly washed with cold water and dried.

**1-(4-Nitrophenyl)-3,3-diphenyltriene (11a):** Yield: 315 mg (99%); m.p. 132 °C (ref. [32]: 127 °C); IR (KBr):  $\bar{\nu}$  = 1588, 1532, 1495, 1457, 1403 (N=N), 1351, 1323, 1303, 1272, 1251, 1141, 1076, 902, 793, 667 cm<sup>-1</sup>; MS (CI, isobutane):  $m/z$ : 319 [M+H]<sup>+</sup>.

**1-(4-Carboxyphenyl)-3,3-diphenyltriene (11b):** Yield: 315 mg (99%); m.p. 222 °C (ref. [32]: 224 °C); IR (KBr):  $\bar{\nu}$  = 1689 (C=O), 1626, 1597, 1552, 1519, 1495, 1385 (N=N), 1300, 1274, 1170, 1137, 899, 868, 834, 746, 691 cm<sup>-1</sup>; MS (CI, isobutane):  $m/z$ : 318 [M+H]<sup>+</sup>.

**1-(4-Chlorophenyl)-3,3-diphenyltriene (11g):** Yield 303 mg (99%); m.p. 123–124 °C (ref. [32]: 122 °C); IR (KBr):  $\bar{\nu}$  = 1597, 1503, 1492, 1483, 1459, 1438, 1393 (N=N), 1283, 1243, 1198, 1171, 1091, 1009, 823, 747, 711, 670 cm<sup>-1</sup>; MS (CI, isobutane):  $m/z$ : 310 (35%), 308 (100%, [M+H]<sup>+</sup>).

**1-(4-Bromophenyl)-3,3-diphenyltriazene (11 h):** Yield: 350 mg (99%); m.p. 48–49 °C (Ref. [32]; 50 °C); IR (KBr):  $\tilde{\nu}$  = 1597, 1503, 1483, 1459, 1418, 1394 (N=N), 1243, 1198, 1171, 1091, 1009, 823 cm<sup>-1</sup>; MS (CI, isobutane):  $m/z$ : 354 (100%), 352 (100%, [M+H]<sup>+</sup>).

**1-(4-Carboxyphenyl)-3-(4-chlorophenyl)triazene (13 g):** Yield: 270 mg (99%); m.p. 187–188 °C (ref. [15]; 188 °C); IR (KBr):  $\tilde{\nu}$  = 1690 (C=O), 1608, 1560, 1542, 1494, 1386 (N=N), 1307, 1290, 1207, 1163, 1116, 1095, 1044, 1017, 822 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>/[D<sub>6</sub>]DMSO):  $\delta$  = 9.6–9.0 (1NH), 8.0–7.2 (m, 8H); MS (CI, isobutane):  $m/z$ : 275 [M+1]<sup>+</sup>; MS (EI):  $m/z$  (%): 237 (2), 149 (2), 137 (100), 127 (40), 120 (79).

**1-(4-Carboxyphenyl)-3-(4-tolyl)triazene (13 i):** Yield: 250 mg (99%); m.p. 181–184 °C (ref. [15]; 183 °C); IR (KBr):  $\tilde{\nu}$  = 1677 (C=O), 1605, 1556, 1504, 1437, 1400 (N=N), 1385, 1311, 1256, 1208, 1164, 848, 821 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>/[D<sub>6</sub>]DMSO):  $\delta$  = 9.8–9.0 (1NH), 8.0–7.1 (m, 8H), 2.20 (s, 3H).

**1-[1-(9,10-Anthraquinone-yl)-3-(4-tolyl)triazene (13 j):** Yield: 339 mg (99%); m.p. 215 °C (ref. [16]; 220–224 °C); IR (KBr):  $\tilde{\nu}$  = 1667 (C=O), 1640 (C=O), 1590, 1544, 1514, 1491, 1461, 1449, 1407 (N=N), 1353, 1306, 1278, 1185, 1167, 1132, 1069, 1011, 926, 825, 810, 734, 709 cm<sup>-1</sup>; MS (CI, isobutane):  $m/z$ : 342 [M+H]<sup>+</sup>.

**1,2-Naphthoquinone-1-(4-nitrophenyl)hydrazone (15 a):**  $\beta$ -Naphthol (173 mg, 1.20 mmol) and 4-nitrophenyldiazonium tetrafluoroborate (**4a'**) (237 mg, Aldrich, 97% purity, 1.00 mmol) were co-ground in an agate mortar six times for 5 min. After being left to rest for 24 h, the mixture was exposed to ultrasound for 24 h. The azo dye tetrafluoroborate was neutralised and excess  $\beta$ -naphthol removed by washing with 0.5 N NaOH (20 mL) and water (20 mL). After drying, pure **15 a** (288 mg, 100%) was obtained; m.p. 248 °C (ref. [33]; 249 °C); IR (KBr):  $\tilde{\nu}$  = 1622 (C=O), 1592, 1500 (NO<sub>2</sub>), 1454, 1330 (NO<sub>2</sub>), 1258, 1226, 1201, 1152, 1106, 1034, 1011, 859, 836, 748 cm<sup>-1</sup>; <sup>1</sup>H NMR (CF<sub>3</sub>COOD):  $\delta$  = 8.69 (d, 1H), 8.60 (d, 2H), 8.21 (d, 1H), 8.07 (d, 2H), 7.82 (m, 2H), 7.70 (t, 1H), 7.17 (d, 1H).

**1,2-Naphthoquinone-1-(phenyl)hydrazone (15 d):**  $\beta$ -Naphthol (77 mg, 0.60 mmol) and phenyldiazonium nitrate (84 mg, 0.50 mmol) were separately ground in an agate mortar, cautiously mixed in a test tube that was stoppered and after 24 h rest exposed to ultrasound for 24 h. The azo dye nitrate was neutralised and excess  $\beta$ -naphthol removed by washing with 0.5 N NaOH (20 mL) and water (20 mL). Pure **15 d** (121 mg, 98%) was obtained; m.p. 132 °C (ref. [34]; 132–133 °C); IR (KBr):  $\tilde{\nu}$  = 1619 (C=O); BLYP: 1607), 1598, 1550 (C=O); BLYP: 1560), 1500 (C=N); BLYP: 1493), 1449, 1385 (C=N); BLYP: 1373), 1268 (N=N); BLYP: 1271), 1255, 1208, 1145, 839, 751 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 8.55 (d, 1H), 7.70 (m, 3H), 7.60–7.25 (m, 6H), 6.87 (d, 1H).

**1,2-Naphthoquinone-1-(4-chlorophenyl)hydrazone (15 g):**  $\beta$ -Naphthol (77 mg, 0.60 mmol) and 4-chlorophenyldiazonium nitrate hydrate<sup>[1]</sup> (110 mg, 0.50 mmol) were separately ground in an agate mortar, cautiously mixed in a closed test tube and after 24 h rest exposed to ultrasound for 24 h. The azo dye nitrate was neutralised and excess  $\beta$ -naphthol removed by washing with 0.5 N NaOH (20 mL) and water (20 mL). Pure **15 g** (141 mg, 99%) was obtained; m.p. 161.5 °C (ref. [35]; 160–161 °C); IR (KBr):  $\tilde{\nu}$  = 1621 (C=O); BLYP: 1607), 1603, 1563 (C=O); BLYP: 1568; 1552), 1484 (C=N); BLYP: 1493), 1450, 1412, 1388 (C=N); BLYP: 1385), 1253, 1210, 1089 (C–Cl); BLYP: 1062), 1006, 985, 821, 749, 680, 497 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 8.59 (d, 1H), 7.80–7.40 (m, 8H), 6.89 (d, 1H); MS (CI, isobutane):  $m/z$ : 285 (35%), 283 (100%, [M+H]<sup>+</sup>).

**1,2-Naphthoquinone-1-(4-bromophenyl)hydrazone (15 h):**  $\beta$ -Naphthol (77 mg (0.60 mmol) and MgSO<sub>4</sub>·2H<sub>2</sub>O (60 mg, 0.50 mmol) as a drying agent were finely ground in an agate mortar. 4-Bromobenzenediazonium nitrate hydrate<sup>[1]</sup> (132 mg, 0.50 mmol) was added in five portions and co-ground for 5 min each. The reaction was completed by 12 h exposure to ultrasound, when all of the diazonium band had disappeared in the IR. The solid material was washed with 0.5 N NaOH (20 mL) and water (20 mL) to yield **15 h** (163 mg, 99%). M.p. 171 °C (ref. [22]; 172–173 °C); IR (KBr):  $\tilde{\nu}$  = 1620 (C=O), 1558, 1505, 821 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 8.50 (d, 1H), 7.71 (d, 1H), 7.59 (m, 6H), 7.40 (t, 1H), 7.86 (d, 1H); MS (CI, isobutane):  $m/z$ : 329 (95%), 327 (100%, [M+H]<sup>+</sup>).

**Solid-state preparation of 5-(4-bromophenylhydrazono)hexahydropyrimidine-2,4,6-triones (18 a–d) and -4,6-dione-2-thione (18 e):** The barbituric acid derivative **16** (0.50 mmol) was ground in an agate mortar. 4-Bromobenzenediazonium nitrate hydrate (**4 h**, 0.50 mmol) was added and co-ground in five portions for 5 min, each. Most of the diazonium band at  $\tilde{\nu}$  = 2280 cm<sup>-1</sup> had disappeared, but completion of the reactions was achieved

by 24 h ultrasound application in a test tube. The solid products were neutralised with 0.5 N NaOH (20 mL), washed with water and dried.

**5-(4-Bromophenylhydrazono)hexahydropyrimidine-2,4,6-trione (18 a):** Yield: 155 mg (100%); m.p. 310–312 °C; IR (KBr):  $\tilde{\nu}$  = 1754, 1707, 1657 (C=O), 1585, 1511, 1490, 1436, 1403, 1385, 1351, 1260, 1174, 1076, 1010, 830, 819, 776, 754 cm<sup>-1</sup>; UV (CH<sub>3</sub>OH):  $\lambda_{\max}$  ( $\epsilon$ ) = 388 (26700 nm); <sup>1</sup>H NMR (CDCl<sub>3</sub>/[D<sub>6</sub>]DMSO):  $\delta$  = 10.75 (bp, 2NH), 8.0 (s, 1NH), 7.48 (AA'BB', 2H), 7.42 (BB'AA', 2H); <sup>13</sup>C NMR (CF<sub>3</sub>COOD):  $\delta$  = 164.94, 164.35, 152.43, 139.35, 133.94 (2C), 125.27, 120.16 (2C), 116.35; MS (70 eV):  $m/z$  (%): 312 (19), 310 (21), 171 (9), 169 (10), 157 (9), 155 (18).

**5-(4-Bromophenylhydrazono)-1,3-dimethylhexahydropyrimidine-2,4,6-trione (18 b):** Yield: 167 mg (99%); m.p. 246–248 °C; IR (KBr):  $\tilde{\nu}$  = 1719, 1672, 1640 (C=O), 1583, 1504, 1444, 1384, 1363, 1274, 1254, 1225, 1197, 1071, 809, 751 cm<sup>-1</sup>; UV (CH<sub>3</sub>OH):  $\lambda_{\max}$  ( $\epsilon$ ) = 390 (28800 nm); <sup>1</sup>H NMR (CDCl<sub>3</sub>/[D<sub>6</sub>]DMSO):  $\delta$  = 7.55 (AA'BB', 2H), 7.40 (BB'AA', 2H), 3.29 (s, 3H), 3.26 (sh, 1NH), 3.25 (s, 3H); <sup>13</sup>C NMR (CF<sub>3</sub>COOD):  $\delta$  = 164.06, 162.9, 152.93, 139.79, 133.73 (2C), 123.51, 119.82 (2C), 115.89, 29.14, 27.77; MS (70 eV):  $m/z$  (%): 340 (15), 338 (21), 183 (10), 173 (70), 171 (94), 157 (7), 155 (8); HR-MS (CI, isobutane) calcd for C<sub>12</sub>H<sub>11</sub>BrN<sub>4</sub>O<sub>3</sub>+H: 339.0140; found 339.0145.

**5-(4-Bromophenylhydrazono)-1,3-diethylhexahydropyrimidine-2,4,6-trione (18 c):** Yield: 182 mg (99%); m.p. 182 °C; IR (KBr):  $\tilde{\nu}$  = 1721, 1650 (C=O), 1585, 1519, 1438, 1410, 1383, 1281, 1237, 1104, 1082, 1071, 956, 824 cm<sup>-1</sup>; UV (CH<sub>3</sub>OH):  $\lambda_{\max}$  ( $\epsilon$ ) = 390 (28600 nm); <sup>1</sup>H NMR (CDCl<sub>3</sub>/[D<sub>6</sub>]DMSO):  $\delta$  = 14.59 (s, 1NH), 7.55 (AA'BB', 2H), 7.44 (BB'AA', 2H), 4.06 (q,  $J$  = 7.0 Hz, 2H), 4.02 (q,  $J$  = 7.0 Hz, 2H), 1.28 (t,  $J$  = 7.0 Hz, 3H); 1.27 (t,  $J$  = 7.0 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>/[D<sub>6</sub>]DMSO):  $\delta$  = 160.65, 158.38, 149.48, 139.79, 132.56 (2C), 119.86, 118.37 (2C), 116.87, 37.04, 36.19, 13.02 (2C); MS (70 eV):  $m/z$  (%): 368 (72), 366 (65), 340 (3), 338 (3), 219 (19), 198 (26), 196 (84), 173 (48), 172 (22), 171 (74), 170 (20), 169 (24), 157 (24), 155 (24), 145 (13), 143 (10), 125 (25); HR-MS (CI, isobutane) calcd for C<sub>14</sub>H<sub>15</sub>BrN<sub>4</sub>O<sub>3</sub>+H: 367.0405; found 367.0405.

**5-(4-Bromophenylhydrazono)-1,3-diphenylhexahydropyrimidine-2,4,6-trione (18 d):** Yield: 228 mg (99%); m.p. 150 °C; IR (KBr):  $\tilde{\nu}$  = 1691, 1655 (C=O), 1517, 1490, 1429, 1404, 1384, 1358, 1294, 1233, 1071, 1005, 943, 825, 741, 693 cm<sup>-1</sup>; UV (CH<sub>3</sub>OH):  $\lambda_{\max}$  ( $\epsilon$ ) = 390 (18700 nm); <sup>1</sup>H NMR (CDCl<sub>3</sub>/[D<sub>6</sub>]DMSO):  $\delta$  = 7.56–7.28 (m, 14H); 4.02 (s, 1NH); MS (70 eV):  $m/z$  (%): 464 (24), 462 (26), 198 (10), 196 (14), 171 (24), 169 (20), 120 (16), 119 (100); HR-MS (CI, isobutane) calcd for C<sub>22</sub>H<sub>15</sub>BrN<sub>4</sub>O<sub>3</sub>+H: 463.0627; found 463.0649.

**5-(4-Bromophenylhydrazono)-1,3-diethyl-2-thioxohexahydropyrimidine-4,6-dione (18 e):** Yield: 189 mg (99%); m.p. 235–237 °C; IR (KBr):  $\tilde{\nu}$  = 1696, 1638 (C=O), 1584, 1516, 1505, 1433, 1405, 1350, 1320, 1303, 1268, 1237, 1104, 1083, 1068, 911, 831 cm<sup>-1</sup>; UV (CH<sub>3</sub>OH):  $\lambda_{\max}$  ( $\epsilon$ ) = 417 (29600 nm); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 14.83 (s, 1NH), 7.56 (AA'BB', 2H), 7.46 (BB'AA', 2H), 4.59 (q,  $J$  = 7.0 Hz, 2H), 4.55 (q,  $J$  = 7.0 Hz, 2H), 1.32 (t,  $J$  = 7.0 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 177.46, 159.31, 157.44, 139.77, 132.91 (2C), 120.83, 118.88 (2C), 117.97; 43.82, 42.65, 12.33, 12.12; MS (70 eV):  $m/z$  (%): 385 (10), 384 (42), 383 (8), 382 (37), 351 (31), 349 (37), 213 (13), 212 (100), 185 (12), 184 (10), 183 (15), 173 (24), 172 (28), 171 (38), 157 (18), 155 (25), 145 (8), 143 (12); HR-MS (CI, isobutane) calcd for C<sub>14</sub>H<sub>15</sub>BrN<sub>4</sub>O<sub>2</sub>S+H: 383.0161; found 383.0159.

**Solid-state synthesis of 4-(arylhydrazono)-4,5-dihydropyrazole-5-ones 21:** 3-Methyl-1-phenyl-4,5-dihydropyrazole-5-one (**19**, 1.00 mmol) and the solid diazonium salt **4a'**, **4f**, **4h** or **6a** (1.00 mmol) were cautiously co-ground in an agate mortar for 5 min. The mixture was transferred to a 100 mL flask which was then evacuated. The mixture was exposed to (CH<sub>3</sub>)<sub>3</sub>N (0.5 bar) for 12 h at room temperature. After condensation of excess gas into a remote trap at 77 K, the trimethylammonium nitrate (tetrafluoroborate) was washed away with water ( $\approx$ 20 mL) and the residual solid dried. The <sup>13</sup>C NMR spectra of **21 a, f, h** have already been reported in Ref. [36].

**4-(4-Nitrophenylhydrazono)-3-methyl-1-phenyl-4,5-dihydropyrazole-5-one (21 a):** Yield from **4a'**: 317 mg (98%); from **6a**: 320 mg (99%); m.p. 197 °C (ref. [24]; 197–198 °C); IR (KBr):  $\tilde{\nu}$  = 1666 (C=O), 1610, 1599, 1558 (C=C, C=N), 1505 (NO<sub>2</sub>), 1342 (NO<sub>2</sub>) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 13.65 (1NH), 8.30 (AA'BB', 2H), 7.98 (BB'AA', 2H), 7.59–7.40 (m, 4H), 7.28 (m, 1H), 2.39 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>/[D<sub>6</sub>]DMSO):  $\delta$  = 155.61, 147.51, 145.49, 143.02, 136.59, 130.09, 127.74 (2C), 124.37 (2C), 124.12, 117.11 (2C), 114.70 (2C), 10.64.

**4-(4-Methoxyphenylhydrazono)-3-methyl-1-phenyl-4,5-dihydropyrazole-5-one (21 f)**: Yield: 305 mg (99%); m.p. 139 °C (ref. [24]: 139–140 °C); IR (KBr):  $\tilde{\nu}$  = 1651, 1610, 1597, 1553, 1487, 1442, 1416, 1364, 1344, 1281, 1244, 1183, 1156 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 13.77 (br, 1NH), 7.98 (AA'BB', 2H), 7.39 (m, 4H), 7.21 (m, 1H), 6.98 (BB'AA', 2H), 3.84 (s, 3H), 2.40 (s, 3H).

**4-(4-Bromophenylhydrazono)-3-methyl-1-phenyl-4,5-dihydropyrazole-5-one (21 h)**: Yield: 350 mg (98%); m.p. 149 °C (ref. [25]: 151 °C); IR (KBr):  $\tilde{\nu}$  = 1659 (C=O), 1587, 1567, 1555 (C=C, C=N), 1501, 1479, 1341, 1254, 1151 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 13.55 (br, 1NH), 7.91 (AA'BB', 2H), 7.60 (m, 2H), 7.29 (BB'AA', 2H), 7.24 (m, 1H), 2.37 (s, 3H).

#### Azocouplings in solution

**15a**: By modification of the procedure given in reference [17]:  $\beta$ -naphthol (1.44 g, 10.0 mmol) and NaOH (0.80 g, 20 mmol) in H<sub>2</sub>O (10 mL) were cooled to 5–10 °C while the stoichiometric quantity of the solid diazonium salt **4a'** (2.44 g, 10.0 mmol of 97% pure material) was added with stirring in small portions over a period of 10 min. After addition of H<sub>2</sub>O (20 mL), the mixture was stirred at room temperature for 16 h. The precipitate was collected by centrifugation, thoroughly washed with water, and dried at 80 °C under vacuum to give a first crop of **15a** (2.358 g; m.p. 247 °C). The dark liquid from the centrifugation and the first washing were salted out with NaCl (5.6 g) to give further **15a** (0.331 g). The mother liquor was dark and still contained more of the dye that did not readily separate, but could probably be isolated from at least three organic impurities by extensive chromatographic techniques. Total yield: 2.689 g (92%).

**18a**: By modification of a general procedure given in reference [17]: a slurry of **16a** (460 mg, 3.6 mmol) and NaOAc (200 mg, 2.4 mmol) in ethanol (7 mL) and water (2 mL) were cooled to 0–5 °C while the stoichiometric quantity of the solid diazonium salt **4h** (950 mg, 3.6 mmol) was added in small portions with stirring over a period of 10 min. After addition of H<sub>2</sub>O (10 mL), the mixture was stirred at room temperature for 20 h. The yellow precipitate was collected by centrifugation, thoroughly washed with water, and dried at 80 °C under vacuum to give **18a**. Yield: 1.117 g (100%); m.p. 310–312 °C.

**21a**: By modification of a general procedure given in reference [17]: Compound **19** (870 mg, 5.0 mmol) and NaOAc (615 mg, 7.5 mmol) in ethanol (10 mL) and water (4 mL) were cooled to 0–5 °C while the stoichiometric quantity of the solid diazonium salt **4a** (1.15 g, 5.0 mmol) was added in small portions with stirring over a period of 10 min. After addition of H<sub>2</sub>O (10 mL), the mixture was stirred at room temperature for 14 h. The precipitate was collected by centrifugation, thoroughly washed with water, and dried at 80 °C under vacuum to give an orange solid (1.529 g, 95%) containing **21a** (92% <sup>1</sup>H NMR). Yield after recrystallisation from ethanol: 81%.

**Preparation of the aryl iodides 23**: KI (830 mg, 5.0 mmol) was finely ground in an agate mortar and the diazonium salt (0.50 mmol) added in five portions and co-ground for 5 min each. After a 24-h hour rest with occasional grinding, the diazonium band in the IR spectra had completely disappeared. The potassium salts were removed by washing with cold water.

**4-Iodonitrobenzene (23a)**: Yield: 124 mg (100%); m.p. 172 °C (ref. [37]: 172–174 °C); IR (KBr):  $\tilde{\nu}$  = 1594, 1571, 1513, 1469, 1411, 1391, 1353, 1340, 1308, 1272, 1178, 1105, 1052, 1008, 851, 837, 735, 674 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.8–8.0 (AA'BB' system); MS (CI, isobutane):  $m/z$ : 250 [M+H]<sup>+</sup>.

**4-Iodobenzoic acid (23b)**: Yield: 123 mg (100%); m.p. 268 °C (ref. [38]: 267–270 °C); IR (KBr):  $\tilde{\nu}$  = 3086, 2983, 2894, 2840, 2726, 2670, 2559, 1932, 1804, 1680, 1588, 1564, 1482, 1426, 1393, 1321, 1295, 1273, 1181, 1127, 1109, 1055, 1008, 932, 850, 812, 755 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.6–7.4 (AA'BB' system); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 167.00, 136.78, 130.53 (2C), 129.89 (2C), 99.53.

**4-Bromiodobenzene (23h)**: Yield 144 mg (100%); m.p. 90 °C (ref. [37]: 90–92 °C); IR (KBr):  $\tilde{\nu}$  = 1883, 1617, 1464, 1372, 1251, 1097, 1064, 995, 800 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.1–7.7 (AA'BB' system).

**1-Iodoanthraquinone (23j)**: Yield: 165 mg (100%); m.p. 203 °C (ref. [39]: 205 °C); IR (KBr):  $\tilde{\nu}$  = 1676, 1591, 1568, 1402, 1315, 1265, 1240, 1157, 1106, 948, 805, 721, 703, 638 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 8.5–8.2 (m, 4H), 7.9–7.6 (m, 2H), 7.5–7.3 (m, 1H); MS (CI, isobutane):  $m/z$ : 335 [M+H]<sup>+</sup>.

**4-Cyanoiodobenzene (23k)**: Yield: 113 mg (100%); m.p. 122–124 °C (ref. [40]: 124–125.5 °C); IR (NaCl):  $\tilde{\nu}$  = 2224 (CN), 1642, 1607, 1581, 1522, 1474, 1446, 1390, 1250, 1170, 1114, 1054, 1008, 818 cm<sup>-1</sup>; MS (CI, isobutane):  $m/z$ : 286 (100%, [M+isobutyl]<sup>+</sup>), 230 (80% [M+H]<sup>+</sup>).

**2-Iodobenzoic acid (23i)**: Yield: 123 mg (100%); m.p. 157–160 °C (ref. [41]: 157.5–159 °C); IR (NaCl):  $\tilde{\nu}$  = 1686, 1582, 1564, 1468, 1304, 1271, 1111, 1047, 1015, 737 cm<sup>-1</sup>; MS (CI, isobutane):  $m/z$ : 249 [M+H]<sup>+</sup>.

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