This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Solid-to-solid Reaction of 2,4-Dinitrophenylhydrazine with Several Aromatic Aldehydes Bearing Electron-donating Groups

Beata Szczesna[a]; Zofia Urbanczyk-lipkowska[a]
[a] Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland

To cite this Article Szczesna, Beata and Urbanczyk-lipkowska, Zofia(2001) 'Solid-to-solid Reaction of 2,4-Dinitrophenylhydrazine with Several Aromatic Aldehydes Bearing Electron-donating Groups', Supramolecular Chemistry, 13: 1, 247 — 251

To link to this Article: DOI: 10.1080/10610270108034897

URL: http://dx.doi.org/10.1080/10610270108034897

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SUPRAMOLECULAR CHEMISTRY, Vol. 13, pp. 247–251
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Solid-to-solid Reaction of 2,4-Dinitrophenylhydrazine with Several Aromatic Aldehydes Bearing Electron-donating Groups*

BEATA SZCZESNA and ZOFIA URBANCZYK-LIPKOWSKA[†]

Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland

Aromatic 2,4-dinitrophenylhydrazones are conveniently prepared from 2,4-dinitrophenylhydrazyne and the corresponding aldehydes bearing electron-donating groups [N(Me)$_2$, OMe and OH] in non-solvent reactions. The high-dilution method in the absence of basic or acidic catalysts is also efficient. According to X-ray data, planar conformation of the hydrazone molecules is stabilized by intramolecular NH... O$_2$N hydrogen bond. Formation of 2D networks in the crystal is mediated *via* intermolecular CH... O$_2$N hydrogen bonds.

Keywords: Non-solvent reaction; 2,4-dinitrophenylhydrazones

2,4-dinitrophenylhydrazine has been used in analytical organic chemistry for characterization of aldehydes and ketones by hydrazones formation [1, 2]. The chemical stability of hydrazones and their high melting points have recently made them attractive as prospective new materials for opto-electronic applications or frequency doubling [3, 4].

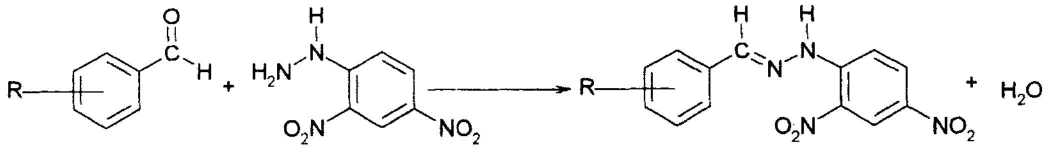
The preparation and solid state structure of new organometallic complexes with the involvement of hydrazones have also been reported [5, 6]. Although hydrazones have been synthesized for over 70 years, structural information on their solid state structure is scarce. The Cambridge Crystallographic Database contains only 14 crystal structures of aromatic hydrazones [7]. In terms of crystal engineering technique, aromatic hydrazones, due to their extended π-conjugated system, offer the possibility of preparation of easily polarizable, planar molecules on functionalization of both phenyl rings. In the classic preparative procedure, hydrazones are made, often with good yield, in solution from hydrazines and aldehydes in the presence of basic or acidic catalysts [8]. However, recently, efficient solid-to-solid reaction between aromatic amines and aromatic aldehydes leading readily to Shiff bases has been reported [9]. This turned our attention to the potential application of this environmentally friendly technique in the present case.

We selected reaction between benzaldehyde substituted with electron-donating groups [$R = p$-N(Me)$_2$, o-OMe or o, m, p-OH] (**1**) and 2,4-dinitrophenylhydrazine (**2**).

---

* Dedicated to Professor Fumio Toda on the occasion of his 67th Birthday.

[†] Corresponding author.



The resulting molecules of hydrazones **3** contain terminal groups with opposite electron donor–acceptor properties and should be planar. That provides an opportunity for the construction of 2D networks that can be useful models for further studies of their arrangement in the third dimension.

RESULTS AND DISCUSSION

A solid state reaction takes place when a finely ground mixture of 2,4-dinitrophenylhydrazine (**2**) and respective aldehyde (**1**) is heated at a temperature 20–50° below one melting point of the aldehyde and occasionally ground again (reaction with liquid salicylaldehyde required better grinding). Taking IR spectra in KBr pellets monitored the reaction progress. Figure 1 shows changes in time of the selected regions of the FT-IR spectra collected for **3e**. All bands on the initial IR spectrum can be assigned to the known bands of *p*-hydroxybenzaldehyde and 2,4-dinitrophenylhydrazine. On further grinding along with mild heating (ca. 50°C for 20′) the original $\nu(NH_2)$ band at $3501\,cm^{-1}$ and $\nu(C{=}O)$ of an aldehyde at $1671\,cm^{-1}$ slowly diminished. Further heating of the reaction mixture for 2 hrs results in the disappearance of the C=O band and the appearance of the C=N band at $1617\,cm^{-1}$. The reaction was completed after 24 hrs. The FT-IR spectrum was the same as for the crystalline product obtained from MeOH without addition of catalyst and the amorphous product obtained by the classic procedure (in EtOH with addition of concentrated H_2SO_4). Typically, reaction takes place in several hours to two days. The reaction yield exceeds 95% as evidenced by IR and NMR spectra taken for crude reaction products. The solid-to-solid reaction rate can be significantly enhanced when a small amount of powdered substrates is mixed with Nujol and heated for 5–30 min. Enhancement of molecular movement in Nujol was observed before during the formation of racemates from powdered enantiomers [10].

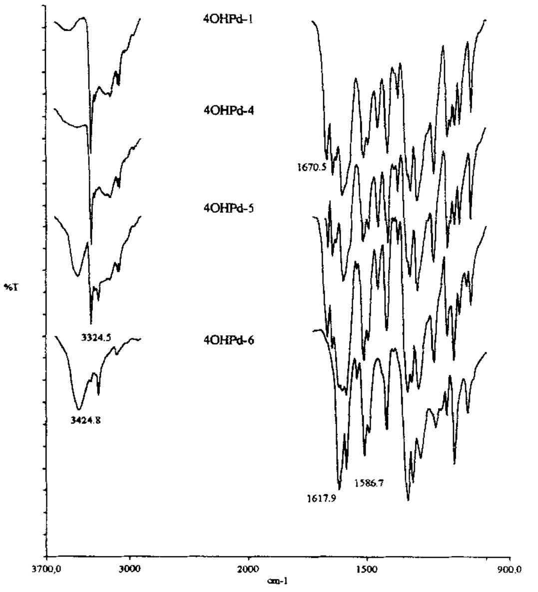


FIGURE 1 Selected areas of FTIR spectra showing formation of **3e** in time: 4OHPD-1 – initial mixture of powdered 2,4-dinitrophenylhydrazine and *p*-hydroxybenzylaldehyde; 4OHPD-4 – hitting for 20 min. in temp. 60°C; 4OHPD-5 – hitting for 2 hrs. in temp. 60°C; 4OHPD-6 – final reaction product after 24 hrs.

The high yield of the solid-to-solid thermal reaction prompted us to compare the yield of product **3** formation in high dilution conditions in the absence of acid or base catalyst. Apparently, well-formed crystals of the products have been obtained in every case, and have been identified as *E* isomers. Reaction was performed in solution by stirring at 50–60°C 1 mmol of 2,4-dinitrophenylhydrazine (**1**) in 100 ml of MeOH with 1 mmol of the respective aldehyde dissolved in 50 ml of MeOH (except compound **3b**, when total reaction volume was 250 ml) for 4 hours. Then the solution was allowed to crystallize. In every case, crystalline hydrazones were formed with reasonable yield. The product has been characterized by solution NMR and X-ray crystal determination as *E* isomer (X-ray structures will be published elsewhere). Thin layer chromatography of reaction products confirmed that the same isomer was formed in both conditions. The crystals of **3** were separated 2–3 times. In the case of **3b** the last fraction was a mixture of two types of crystals with different color and crystal habit. X-ray structure analysis showed that abundant crystals contained the desired reaction product, whereas several tear-shaped yellow crystals were reaction product with acetone (**3b′**) from impurities contained in MeOH. As might be seen in Figures 2 and 3, an intramolecular NH...O_2N hydrogen bond stabilizes planar conformation of the molecules. Molecules of **3b** form 2D polar networks glued by intermolecular CH...O_2N hydrogen bonds formed by both nitro groups. Neighboring planes, however, contain molecules aligned in opposite directions, so the resultant space group is centrosymmetric. Molecules of the reaction product with acetone **3b′** form hydrogen-bonded centrosymmetric dimers further aligned in tapes.

The possibility of the formation of another crystal form was checked when crystals of the reagents containing excess aldehyde **1e** were heated between two thin-glass slides under the microscope. The reaction was stable up to 108°C when the trace of water evaporated, followed by melting of the aldehyde at 112°. At 150° the liquid part became orange due to hydrazine desolvation and thin flaky crystals appeared. Several large yellow needles sublimed at the upper glass slide at ca. 230°, and at 240° all of the product was crystalline. Finally, yellow needles melted at 278° and the remaining dark orange crystals at 284–286°. According to the literature data the yellow needles might be **3e**

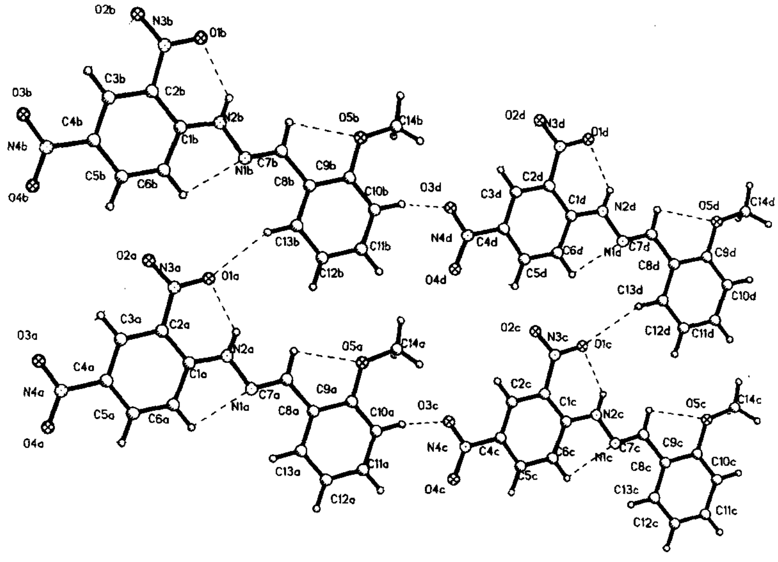


FIGURE 2 Formation 2D network by intermolecularly H-bonded molecules of *N*-(2,4-dinitrophenyl)-*N′*-(2-methoxybenzylidene)-hydrazine, **3b**.

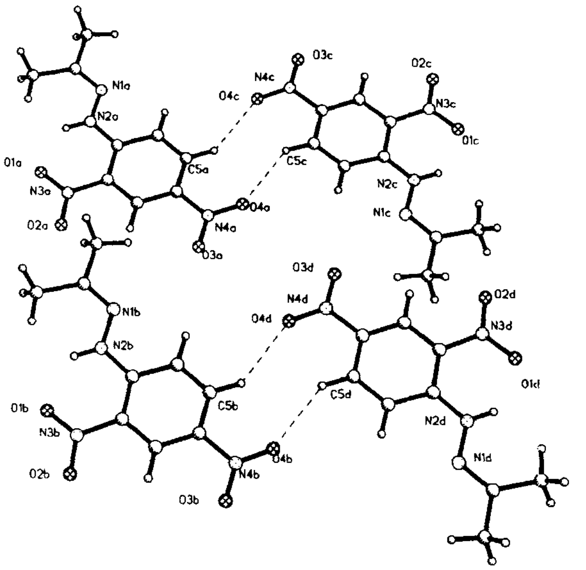


FIGURE 3 Formation of 2D tapes by intermolecularly H-bonded molecules of *N*-(2,4-dinitrophenyl)-*N*′-(isopropylidene)-hydrazine, **3b**′.

monohydrate [11]. This result and the slightly different melting points found for compound **3e** crystallized from various solvents might explain the wide range of literature data on melting temperatures of hydrazones. Possible formation of clathrates containing solvent molecules was further confirmed by X-ray structure of **3e** crystallizing with one molecule of MeCN.

EXPERIMENTAL

General Procedures

Infrared spectra were recorded on Perkin Elmer 16400 Fourier Transform Infrared Spectrophotometer in KBr pellet and Nujol. Melting points were determined on a Kofler hot stage apparatus and are uncorrected. ^{1}H-NMR spectra were recorded using a Bruker AM 500 (500 MHz) and ^{13}C-NMR spectra also using a Bruker AM 500 (125 MHz) in DMSO(d_6). The crystals of the compounds **3b** and **3b**′ were obtained directly from reaction in MeOH and used without recrystallization. Intensity data were collected on a Nonius BV MACH3 diffractometer at 294 K using graphite monochromated CuK$_\alpha$ radiation and ω-2θ scan mode. Refined unit cell parameters were obtained by least-squares analysis of 25 reflections (θ-range 23.2–43.2°) and 15 reflections (θ-range 9.02–23.65°) for compound **3b** and **3b**′, respectively.

Preparation of Aromatic Hydrazones in Solid-to-solid Reaction

Powdered samples of 2,4-dinitrophenylhydrazine and the respective aldehyde were ground in an agate mortar with a pestle for 15 min. Then the mortar was covered with a glass plate and heated at 40–60°C until the reaction was completed (12 h, 4 h, 12 h, 112 h and 24 h) for compounds **3a**, **3b**, **3c**, **3d** and **3e**, respectively. The resulting products were used without further purification or recrystallization. Thin layer chromatography, ^{1}H NMR, 13C NMR and IR spectra evidenced formation of the respective hydrazones with yields exceeding 95%. All products are known compounds.

Preparation of Aromatic Hydrazones in Solution

Reaction was performed in solution by stirring 1 mmol of 2,4-dinitrophenylhydrazine (**1**) in 100 ml of MeOH with 1 mmol of the respective aldehyde dissolved in 50 ml of MeOH at ca. 60°C (except compound **3b**, when total reaction volume was 250 ml). Then the solution was left for crystallization. Crystalline product was collected 2, 3 times and characterized by comparison of melting points and IR spectra with literature data.

Structure Solution and Refinement

The crystal structures were solved by direct methods using the program SHELXS-86 [12] and

TABLE I Yields and melting points for products **3** obtained by solid–solid and solution (MeOH) method

Compound	Solid–solid m.p (°C)	Solution m.p. (°C)	Yield (%)
3a, $R = p$-N(Me)$_2$	236–237	237–239	63
3b, $R = o$-OMe	239–241	247–248	94[1]
3c, $R = o$-OH	257–260	262–265	83
3d, $R = m$-OH	258–261	262–265	61
3e, $R = p$-OH	279–283	284–286[2]	82

[1] 3rd fraction of crystals contained small amount of reaction product with acetone, **3b′**.
[2] –crystals from MeCN/MeOH: at 149° became opaque and melted at 282–286°.
–crystals from $CHCl_3$ melt at 279–281°.
–crystals from AcOEt melt at 263–265°.

refined by full-matrix, least-squares procedure using the program SHELXL-97 [13]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically generated positions and refined with positional parameters riding on the host atom, and B_{iso} fixed at 20% higher than that of the host atom. Crystal data and other experimental details regarding structure solution and refinement are given in Table II. Final fractional coordinates, temperature factors, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

TABLE II Crystal data and structure refinement for **3b** and **3b′**

	3b	**3b′**
Crystal data		
Empirical formula	$C_{14}H_{12}N_4O_5$	$C_9H_{10}N_4O_4$
Formula weight	316.28	238.21
Space group	P(−)1	P(−)1
a (Å)	7.2472(6)	7.1930(10)
b (Å)	7.7454(6)	8.271(2)
c (Å)	14.1058(5)	10.118(2)
α (°)	97.838(4)	66.70(3)
β (°)	96.511(5)	89.43(3)
γ (°)	110.931(6)	79.20(3)
V (Å^3)	721.30(9)	541.69(19)
Z	2	2
D_c (g cm^{-3})	1.456	1.460
μ(CuK$_\alpha$)	0.964	1.006
F(000)	328	248
Data collection		
Crystal size (mm)	0.67 × 0.32 × 0.21	0.14 × 0.105 × 0.43
θ-range (°)	3.21 to 74.02	4.77 to 74.00
Index ranges	−9, ± 9, ± 17	± 8, 10, ± 12
Refl. collected	2242	1866
Final refinement		
No. refl. indep.	2057	1743
No. parameters	217	159
R indices [I > 2σ(I)]	$R_1 = 0.0680$, $wR_2 = 0.1608$	$R_1 = 0.0658$, $wR_2 = 0.1898$
R indices (all data)	$R_1 = 0.0695$, $wR_2 = 0.1633$	$R_1 = 0.0664$, $wR_2 = 0.1907$
$\Delta\rho$max	0.329	0.331
$\Delta\rho$min	−0.376	−0.365

References

[1] Allen, C. F. H. (1930). *J. Am. Chem. Soc.*, **52**, 2955.
[2] Brady, O. L. (1931). *J. Chem. Soc.*, p. 756.
[3] Pan, F., Bosshard, Ch., Wong, M. S., Serbutoviez, C., Follonier, S., Günter, P., Schenk, K. (1996). *J. Cryst. Growth*, **165**, 273.
[4] Liakatas, I., Wong, M. S., Gramlich, V., Bosshard, Ch., Günter, P. (1998). *Adv. Mater.*, **10**, 777.
[5] Granell, J., Moragas, R., Sales, J., Font-Bardia, M., Solans, X. (1993). *J. Chem. Soc., Dalton Trans.*, p. 1237.
[6] Adams, C. J., Bruce, M. I., Dickworth, P. A., Humprey, P. A., Kuhl, O., Tiekink, E. R. T., Cullen, W. R. (1994). *J. Organomet. Chem.*, **467**, 251.
[7] Cambridge Structural Database, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, England, 1999.
[8] Vogel, R. (1989). Text Book of Practical Organic Chemistry, 5th edn., John Wiley and Sons Inc., New York.
[9] Schmeyers, J., Toda, F., Boy, J., Kaupp, G. (1998). *J. Chem. Soc. Perkin Trans.*, **2**, 989.
[10] Toda, F., Tanaka, K., Miyamoto, H., Koshima, H., Miyahara, I., Hirotsu, K. (1997). *J. Chem. Soc., Perkin Trans.*, **2**, 1877.
[11] Dagley, S., Pattel, M. D. (1957). *Biochem. J.*, **66**, 227.
[12] Sheldrick, G. M. (1985). SHELX-86, *Crystallographic Computing*, **3**, Eds. Sheldrick, G. M., Kruger, C. and Goddard, R., Oxford University Press, p. 175.
[13] Sheldrick, G. M. (1997). SHELXL-97, Program for Crystal Structures Refinement, University of Göttingen, Germany.