

Halogen-bonding in 3-nitrobenzaldehyde-derived dichlorodiazadienes

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In honor of Professor Lanny Liebeskind

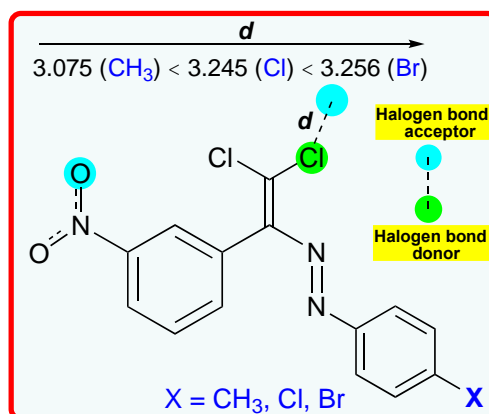
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Abstract

A set of 4,4-dichloro-1,2-diazabutadienes derived from 3-nitrobenzaldehyde was prepared by the copper catalyzed reaction of the corresponding hydrazones with CCl_4 in the presence of TMEDA. The structure of all products was confirmed by ^1H and ^{13}C NMR spectra and ESI-MS. X-ray diffraction revealed $\text{Cl}\cdots\text{O}$ halogen binding in the crystal form for some dienes. Moreover, $\text{Br}\cdots\pi$ and $\text{Cl}\cdots\pi$ types of halogen bonds are observed. Azo dyes absorb in the UV-Vis region with the λ_{max} located at about 234–437 nm in CH_2Cl_2 , DMF and MeOH. Both absorption intensity and λ_{max} is dependent on the solvent polarity and the electron-withdrawing/donating ability of *para*-substituents on the aromatic moiety of the dichlorodiazadienes.

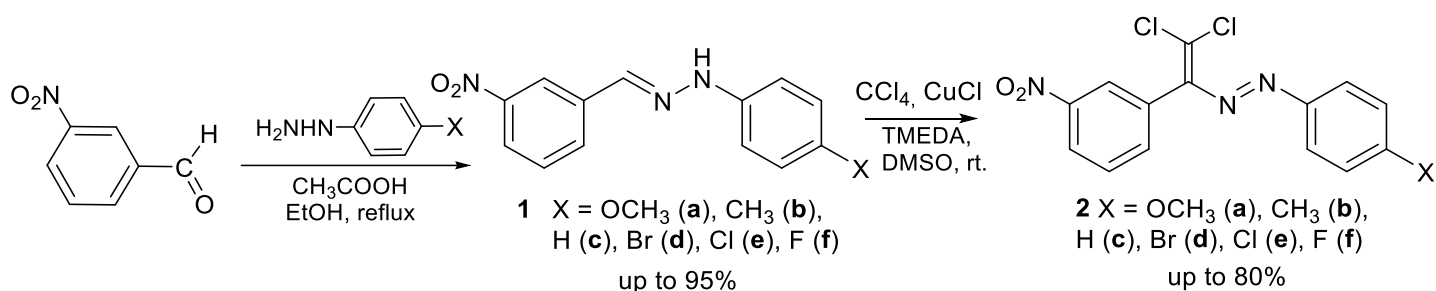


Keywords: Weak interactions, halogen bonding; hydrogen bonding; azo dyes, olefination

Introduction

Azo dyes R–N=N–R (R = aryl, heterocycle, etc.) are a well-known class of organic compounds in synthetic chemistry. They have been extensively used for ink jet printing, as food additives, for dyeing textiles, as indicators, cosmetics, in non-linear optics and dye-sensitized solar cells, as pigments, radical reaction initiators, photo-sensitizers, and therapeutic agents, etc.^{1–5} Due to the industrial applications of azo dyes, the –N=N– fragment has been incorporated into polymers and supramolecular compounds to show valuable properties and the possibility of fine-tuning by variation of R.^{6,7} There are many synthetic strategies for the synthesis of azo compounds, but the well-established method is azo-coupling of an aryl diazonium cation with another aryl ring, especially those substituted with electron-donating groups.^{1,2} Recently, some of us have developed a new method for the synthesis of azo dyes, namely a copper-catalyzed transformation of N-substituted hydrazones into halogenated azabutadienes.⁸ The attached reactive olefin moiety can contribute to π -conjugation in the design of functional materials or used for further functionalization of dyes.

Due to high directionality, halogen bonding has been used in the design of materials, catalysis and crystal engineering similarly to chalcogen⁹ and pnictogen bonds.^{10–15} Halogen bonding is also an effective strategy to control molecular recognition in solution.¹⁶ The study of halogen-bonded associates has become one of the most attractive areas of research in the solution chemistry.¹⁷ However, to the best of our knowledge, the role of halogen bonding in azo chemistry remains unexplored in spite of high activity in this field.^{18–22} Herein, we demonstrate that this type of noncovalent interaction is of great importance in the design of diazadienes in terms of their intermolecular halogen bond strength (Scheme 1). The *para*-substituents on the aromatic moiety range from typical electron-withdrawing (–Br, –Cl and –F) to typical electron-donating groups (–OCH₃ and –CH₃).



Scheme 1. Synthesis of diazadienes **2**.

Results and Discussion

A set of hydrazones **1** was prepared by the reaction of 3-nitrobenzaldehyde with hydrochlorides of 4-substituted aryl hydrazines (Scheme 1). The reaction was performed in the presence of CH₃COONa in EtOH at 80 °C [see Electronic Supplementary Information (ESI)]. Next, the reaction of **1** with CCl₄ in the presence of CuCl and tetramethylethylenediamine (TMEDA) in DMSO permitted synthesis of the corresponding dichlorodiazadienes **2**. The prepared dienes **2** were isolated as *E*-isomers in up to 80 % yield (see ESI). The structures of all products were confirmed by ¹H and ¹³C NMR spectra and ESI-MS. All diazadienes **2** have characteristic signals in their ¹³C NMR spectra at 123–125 ppm which are typical for these compounds.⁸ The peaks corresponding to the aryl rings of dienes **2** were found in the NMR spectra. In addition, X-ray data were

obtained for some products (Figure 1). Single crystal X-ray analyses of **2b**, **2d** and **2e** show that the 3-nitroaromatic moiety rotates around the C1–C7 bond with dihedral angles of $65.0(5)^\circ$ C6–C1–C7–N1, $114.0(2)^\circ$ C2–C1–C7–N1 and $115.4(2)^\circ$ C2–C1–C7–N1 respectively, whereas azo N=N and olefin C=C fragments are quasi planar with small deviations (Figure 1). Compounds **2b**, **2d** and **2e** contain the C–Cl \cdots O type of intermolecular halogen bonds with distances of 3.075(4), 3.256(3) and 3.245(2) Å, respectively, which are shorter than the sum of the Bondi's Van der Waals radii of the interacting atoms (Cl + O = 1.75 + 1.52 = 3.30 Å²³) (Figure 2). An attachment of halogen bond donor centers Br or Cl to the *para*-position of the aromatic moiety of **2d** and **2e** lead to Br \cdots π or Cl \cdots π types of intermolecular interactions with distances of 3.900 and 3.873 Å, respectively (Figure 2). Besides, the intermolecular Cl \cdots O, Br \cdots π and Cl \cdots π types of halogen bonds, all structures are stabilized by multiple weak intermolecular hydrogen bonds.

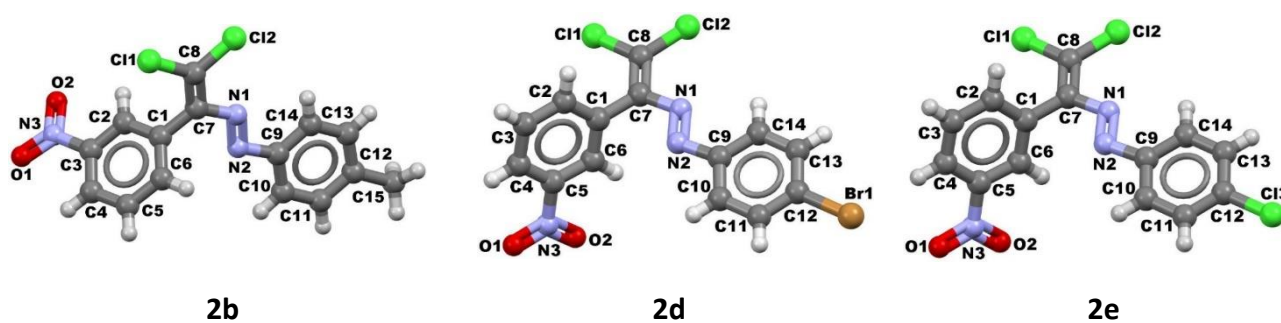


Figure 1. Molecular structures of **2b**, **2d** and **2e** (50% ellipsoids) along with the atomic numbering schemes.

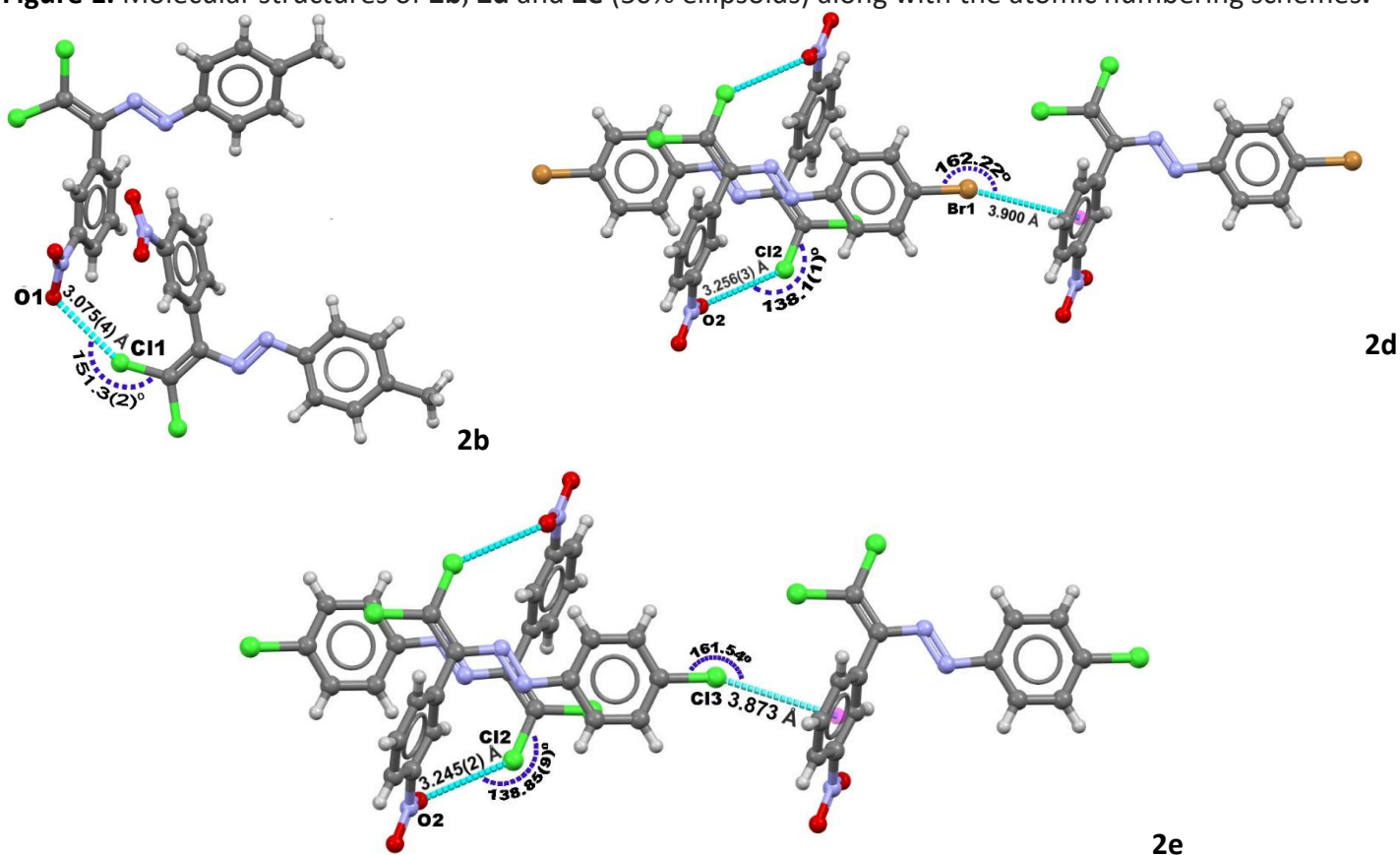


Figure 2. Intermolecular halogen bonds in **2b**, **2d** and **2e** (shown as dashed light blue line).

Table. Absorption maxima (λ_{\max}) of **2** in CH₂Cl₂ (a), DMF (b) and MeOH (c)

	CH ₂ Cl ₂	DMF	MeOH	σ_p^{28d}
2a	260	234	251	-0.27
	370	345	322	
	409	391	387	
2b	305	247	236	-0.17
	357	320	304	
	428	377	398	
2c	300	260	270	0.00
	360	321	308	
	429	360	395	
2d	304	265	250	0.23
	369	320	282	
	437	372	390	
2e	270	261	245	0.23
	368	315	264	
	431	370	390	
2f	267	256	237	0.06
	355	297	264	
	421	349	361	
ϵ^a	41	44	55	
α^b	0.13	0.00	0.98	
β^c	0.10	0.69	0.66	

^a Electric permittivity; ^b H-bond donating ability of solvent;²⁴ ^c H-bonding acceptor ability of solvent.²⁴ ^d Hammett substituent constant.

UV-visible absorption spectra of dyes **2** were recorded over the wavelength range of 200–500 nm, in different solvents [dichloromethane (CH₂Cl₂), dimethylformamide (DMF) and methanol (MeOH)] with different polarity indices, at 298 K and a concentration of 1.00·10⁻⁶ mol L⁻¹ (Table, Figure 3). Three absorption peaks were observed for all compounds (Figure 3), which are significantly influenced by the polarity, H-bond donor or H-bond acceptor ability (α or β)²⁴ of the organic solvents and the electron-withdrawing or electron-donating character of the substituents.²³ The shortest wavelength peak observed in the range of 234–305 nm can be assigned to the excitation of the π -electrons within the C=C bonds in the olefin moieties.^{26–29} The second UV absorption peaks around 355–370 (in CH₂Cl₂), 297–345 (in DMF) and 264–322 (in MeOH) nm (Table) can be attributed to the $\pi \rightarrow \pi^*$ transition in the aromatic rings.^{26–29} The third maxima in the UV spectra of **2a–2f** in the range 409–437 (in CH₂Cl₂), 349–391 (in DMF) and 361–398 (in MeOH) nm can be attributed to the $n \rightarrow \pi^*$ transition in N=N bonds as well as intermolecular hydrogen, Cl \cdots O, Br \cdots π or Cl \cdots π types of halogen bonds. The absorption intensity of the studied dyes increases with a decrease of the solvent polarity, MeOH <

DMF < CH₂Cl₂ (Figure 3), featuring a short energy gap between two states (ground and excited state) with strong intermolecular halogen bonding in CH₂Cl₂, whereas there is no clear trend/correlation between λ_{\max} and σ_p of *para*-substituents.

Conclusions

A set of (*E*)-1-(2,2-dichloro-1-(3-nitrophenyl)vinyl)-2-(*para*-substituted phenyl)diazenes **2** was synthesized by Cu-catalysed olefination of the corresponding N-aryl hydrazones with CCl₄ in the presence of TMEDA in DMSO. Depending on the attached *para*-substituents in the N-aryl fragment, Cl \cdots O, Br \cdots π and Cl \cdots π types of halogen bonds were found in these dyes. The UV spectra of **2** showed three λ_{\max} in CH₂Cl₂, DMF and MeOH, which can be attributed: *i*) the excitation of the π -electrons within the C=C bonds; *ii*) the $\pi \rightarrow \pi^*$ transition in the aromatic rings; *iii*) the $n \rightarrow \pi^*$ transition in N=N bonds as well as intermolecular halogen and hydrogen bonds. The electron-donating or -withdrawing character of *para*-substituents on the aromatic moiety was found to have significant impacts on optical properties of **2**. According to the obtained results we can conclude that the attached halogen bond donor centers on dye molecules **2** may be useful for molecular recognition and design of functional materials.³⁰⁻³⁵

Experimental Section

General. All the chemicals were obtained from commercial sources (Aldrich) and used as received. Infrared spectra (4000–400 cm⁻¹) were recorded on a Vertex 70 (Bruker) instrument in KBr pellets. Carbon, hydrogen, and nitrogen elemental analyses were carried out using a 2400 CHN Elemental Analyzer (Perkin Elmer). The ¹H and ¹³C NMR spectra were recorded on Bruker Advance II+ 300.13 (75.468 carbon-13) MHz (UltraShield™ Magnet) spectrometer at ambient temperature. Chemical shifts are reported in ppm using tetramethylsilane as the internal reference. Electrospray mass spectra (ESI-MS) were run with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 p.s.i. nebulizer pressure. Scanning was performed from *m/z* 0 to 1100 in methanol solution. The compounds were observed in the positive mode (capillary voltage = 80–105 V). The UV-vis absorption spectra in the 200 – 500 nm regions were recorded with a scan rate of 240 nm·min⁻¹ by using a Lambda 35 UV-vis spectrophotometer (Perkin-Elmer) in 1.00 cm quartz cells at room temperature, with a concentration of **2a-2f** of 1.00·10⁻⁶ mol L⁻¹ in CH₂Cl₂, DMF or MeOH.

X-ray structure determinations. X-ray diffraction patterns of **2b**, **2d** and **2e** were collected using a Bruker SMART APEX-II CCD area detector equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 296(2) K, respectively. Absorption correction was applied by SADABS [s1,s2]. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using Bruker's SHELXTL-97 [s3]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were inserted at calculated positions. The details of the crystallographic data for **2b**, **2d** and **2e** are summarized in Table 1. Crystallographic data for the structural analysis have been deposited to the Cambridge Crystallographic Data Center (CCDC 1897671 for **2b**, 2019413 for **2d** and 2019414 for **2e**). Copy of this information can be obtained free of charge from The Director, CCDC,

12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk/data_request/cif).

Synthesis of 1a-1f

A mixture of 3-nitrobenzaldehyde (10 mmol), CH₃COONa (10 mmol), EtOH (50 mL) and the corresponding (*para*-substituted aryl hydrazine hydrochloride (10.2 mmol) was heated at reflux at 80 °C with stirring for 2 h. The reaction mixture was cooled to rt and H₂O (50 mL) was added to give a precipitate of crude product, which filtered off, washed with diluted EtOH (1:1 with water) and dried in vacuo on a rotary evaporator.

(E)-1-(4-Methoxyphenyl)-2-(3-nitrobenzylidene)hydrazine (1a). Red solid (90 %); mp 125-129 °C, lit 130.5 °C.³⁶ Anal. Calcd for C₁₄H₁₃N₃O₃ (*M* = 271.28): C, 61.99; H, 4.83; N, 15.49; found: C, 61.98; H, 4.80; N, 15.47 %. ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.51 (s, 1H, NH), 8.40 (s, 1H, CH), 6.89-8.08 (8H, Ar), 3.70 (s, 3H, OCH₃). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 153.5, 148.8, 139.2, 138.6, 132.9, 131.7, 130.5, 122.0, 119.7, 115.1, 113.8, 55.7.

(E)-1-(3-Nitrobenzylidene)-2-(*p*-tolyl)hydrazine (1b). Yellow solid (91 %); mp 146-150 °C, lit 150.5 °C.³⁶ Anal. Calcd for C₁₄H₁₃N₃O₂ (*M* = 255.28): C, 65.87; H, 5.13; N, 16.46; found: C, 65.80; H, 5.10; N, 16.44 %. ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.59 (s, 1H, NH), 8.41 (s, 1H, CH), 7.00-8.09 (8H, Ar), 2.22 (s, 3H, CH₃). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 148.8, 142.9, 138.5, 1335, 131.8, 130.5, 130.1, 128.5, 122.2, 119.8, 112.7, 20.7.

(E)-1-(3-Nitrobenzylidene)-2-phenylhydrazine (1c). Yellow solid (85 %); mp 119-120, lit 120-124 °C.³⁷ Anal. Calcd for C₁₃H₁₁N₃O₂ (*M* = 241.25): C, 64.72; H, 6.81; N, 17.03; found: C, 64.70; H, 6.79; N, 17.01 %. ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.70 (s, 1H, NH), 8.43 (s, 1H, CH), 6.80-8.09 (9H, Ar). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 148.8, 145.2, 138.3, 134.2, 132.0, 130.6, 129.7, 122.4, 120.0, 119.9, 112.7.

(E)-1-(4-Bromophenyl)-2-(3-nitrobenzylidene)hydrazine (1d). Orange solid (94 %); mp 151-152 °C. Anal. Calcd for C₁₃H₁₀BrN₃O₂ (*M* = 320.15): C, 48.77; H, 3.15; N, 13.13; found: C, 48.75; H, 3.13; N, 13.10 %. ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.81 (s, 1H, NH), 8.44 (s, 1H, CH), 7.09-8.13 (8H, Ar). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 148.7, 144.5, 138.0, 135.2, 132.3, 132.1, 130.6, 122.7, 120.2, 114.7, 110.8.

(E)-1-(4-Chlorophenyl)-2-(3-nitrobenzylidene)hydrazine (1e). Yellow (80 %); mp 147-149 °C, lit 153 °C.³⁶ Anal. Calcd for C₁₃H₁₀ClN₃O₂ (*M* = 275.69): C, 56.64; H, 3.66; N, 15.24; found: C, 56.62; H, 3.56; N, 15.19 %. ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.81 (s, 1H, NH), 8.45 (s, 1H, CH), 7.14-8.13 (8H, Ar). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 148.8, 144.2, 138.0, 135.1, 132.1, 130.6, 129.5, 123.1, 122.7, 120.2, 114.2.

(E)-1-(4-Fluorophenyl)-2-(3-nitrobenzylidene)hydrazine (1f). Orange solid (95 %); mp 133-135 °C. Anal. Calcd for C₁₃H₁₀FN₃O₂ (*M* = 259.24): C, 60.23; H, 3.89; N, 16.21; found: C, 60.17; H, 3.87; N, 16.14 %. ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.68 (s, 1H, NH), 8.43 (s, 1H, CH), 7.09-8.09 (8H, Ar). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 148.8, 141.9, 138.3, 134.2, 132.0, 130.6, 122.4, 120.0, 116.3, 116.0, 113.8.

Synthesis of 2a-2f

A 20 mL screw neck vial was charged with DMSO (10 mL), hydrazone (1 mmol), tetramethylethylenediamine (TMEDA) (295 mg, 2.5 mmol), CuCl (2 mg, 0.02 mmol) and CCl₄ (20 mmol, 10 equiv). After 1-3 hours (until TLC analysis showed complete consumption of corresponding Schiff base) the reaction mixture was poured into ~0.01 M solution of HCl (100 mL, ~pH=2-3), and extracted with CH₂Cl₂ (3 x 20 mL). The combined organic phase was washed with H₂O (3x50 mL), brine (30 mL), dried over anhydrous Na₂SO₄ and concentrated in vacuo of the rotary evaporator. The residue was purified by column chromatography on silica gel using appropriate mixtures of hexane and CH₂Cl₂ (3/1-1/1), and the corresponding diazenes **2a-2f** were obtained.

1-(2,2-Dichloro-1-(3-nitrophenyl)vinyl)-2-(4-methoxyphenyl)diazene (2a). Yellow solid (69 %); mp 142-145 °C. Anal. Calcd for C₁₅H₁₁Cl₂N₃O₃ (*M* = 352.17): C, 51.16; H, 3.15; N, 11.93; found: C, 51.13; H, 3.10; N, 11.89 %. ¹H NMR (300 MHz, CDCl₃): δ 6.97-8.31 (8H, Ar), 3.89 (s, 3H, OCH₃). ¹³C NMR (75 MHz, CDCl₃): δ 150.1, 148.1, 147.1, 145.0, 136.4, 129.1, 125.5, 124.3, 123.6, 120.2, 119.0, 114.3, 55.7. ESI-MS: *m/z*: 353.11 [*M*+H]⁺.

(E)-1-(2,2-Dichloro-1-(3-nitrophenyl)vinyl)-2-(p-tolyl)diazene (2b). Red solid (80 %); mp 140-142 °C, lit. 141 °C.³⁸

1-(2,2-Dichloro-1-(3-nitrophenyl)vinyl)-2-phenyldiazene (2c). Red solid (70 %); mp 125-128 °C, lit. 125-126 °C.⁸ Anal. Calcd for C₁₄H₉Cl₂N₃O₂ (M = 322.15): C, 52.20; H, 2.82; N, 13.04; found: C, 52.14; H, 2.77; N, 12.97 %. ¹H NMR (300 MHz, CDCl₃): δ 7.44-8.32 (9H, Ar). ¹³C NMR (75 MHz, CDCl₃): δ 152.5, 150.2, 148.1, 144.1, 139.8, 136.4, 134.2, 132.1, 129.2, 125.4, 123.7, 123.3. ESI-MS: m/z: 322.08 [M+H]⁺.

(E)-1-(4-Bromophenyl)-2-(2,2-dichloro-1-(3-nitrophenyl)vinyl)diazene (2d). Red solid (68 %); mp 111-113 °C. Anal. Calcd for C₁₄H₈BrCl₂N₃O₂ (M = 401.04): C, 41.93; H, 2.01; N, 10.48; found: C, 41.86; H, 2.01; N, 10.38 %. ¹H NMR (300 MHz, CDCl₃): δ 7.53-8.32 (8H, Ar). ¹³C NMR (75 MHz, CDCl₃): δ 162.3, 151.2, 150.3, 148.1, 137.5, 136.3, 133.9, 132.5, 129.3, 126.8, 125.3, 124.8. ESI-MS: m/z: 402.01 [M+H]⁺.

(E)-1-(4-Chlorophenyl)-2-(2,2-dichloro-1-(3-nitrophenyl)vinyl)diazene (2e). Red solid (64 %); mp 109-110 °C. Anal. Calcd for C₁₄H₈Cl₃N₃O₂ (M = 356.59): C, 47.16; H, 2.26; N, 11.78; found: C, 47.10; H, 2.20; N, 11.74 %. ¹H NMR (300 MHz, CDCl₃): δ 7.21-8.10 (8H, Ar). ¹³C NMR (75 MHz, CDCl₃): δ 150.7, 150.1, 147.9, 137.849, 136.3, 133.7, 132.2, 130.3, 129.3, 125.0, 124.4, 123.7. ESI-MS: m/z: 357.34 [M+H]⁺.

(E)-1-(2,2-Dichloro-1-(3-nitrophenyl)vinyl)-2-(4-fluorophenyl)diazene (2f). Red solid (52 %); mp 100-103 °C. Anal. Calcd for C₁₄H₈Cl₂FN₃O₂ (M = 340.14): C, 49.44; H, 2.37; N, 12.35; found: C, 49.38; H, 2.30; N, 12.27 %. ¹H NMR (300 MHz, CDCl₃): δ 7.12-8.33 (8H, Ar). ¹³C NMR (75 MHz, CDCl₃): δ 151.7, 146.3, 143.8, 136.3, 129.2, 125.6, 125.4, 125.4, 123.8, 121.3, 116.4, 116.1. ESI-MS: m/z: 341.09 [M+H]⁺.

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