Synthesis and Reactions of 1,1-Diiododinitroethylene

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The nitration of tetraiodoethylene gave 1,1-diiododinitroethylene (1). X-ray crystallography showed that one of the two nitro groups is perpendicular to the ethylene plane. Simple amines (dimethylamine, propylamine, aniline) reacted with 1 to give 1,1-diamino-2,2-dinitroethylene derivatives; diamines (*o*-phenylenediamine, ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane) gave the corresponding cyclic products, and a tetramine [(tetrakis(aminomethyl)methane] gave the analogous spiro derivative. Ammonia gave only ammonium cyanodinitromethide, whereas phenol gave 1,1-dinitro-2,2,2-triphenoxyethane. The reaction of 1 with potassium nitrite gave the dipotassium salt of tetranitroethane. X-ray crystallography of the 1,1-diamino-2,2-dinitroethylenes showed twisted olefins, some with twist angles greater than any previously reported for twisted ethylenes, with concomitant bond-distance distortions.

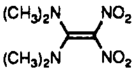
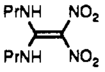
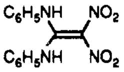
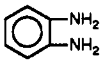
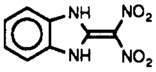
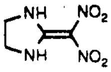
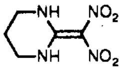
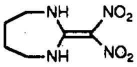
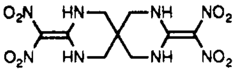
There is current interest in the structural properties[1] as well as synthetic applications[2] of nitro olefins and other electronegatively substituted olefins. Tetranitroethylene[3] has been synthesized by the thermal extrusion of nitrogen tetroxide from hexanitroethane, and recently, we have applied the same reaction for the preparation of 1,2-difluorodinitroethylene from 1,2-difluoro-1,1,2,2-tetranitroethane.[4] X-ray crystallography of 1,2-difluorodinitroethylene showed that one of the two nitro groups is out of the plane of the rest of the molecule and that the C–C double bond distance is unusually short at 1.284 Å. A similar extrusion reaction has been used for the preparation of 1,2-dichlorodinitroethylene from 1,2-dichloro-1,1,2,2-tetranitroethane.[5] Another example of a 1,2-dihalodinitroethylene, 1,2-diiododinitroethylene, was reported by Biltz in 1900 by the nitration of tetraiodoethylene.[6] The present work was undertaken with the objective of studying the properties of 1,2-diiododinitroethylene.

Structure of Diiododinitroethylene. Repetition of the nitration reaction of Biltz gave a material with mp 68–70 °C, as reported.[6] The material was originally identified only by elemental analysis and molecular weight. The ^{13}C NMR spectrum was found to consist of two peaks at 24.8 and 157.3 ppm. Although 1,2-diiododinitroethylene could be expected to show two signals as a mixture of cis and trans isomers, this large difference in chemical shift is not consistent with the structure. This ^{13}C NMR spectrum suggested that the compound is 1,1-diododinitroethylene (1), rather than the 1,2-isomer.

$$(NO_2)IC{=}CI(NO_2) \nleftarrow I_2C{=}CI_2 \xrightarrow{HNO_3} \underset{1}{I_2C{=}C(NO_2)_2}$$

This assignment was confirmed by single-crystal X-ray diffraction analysis (Figure 1). There are two molecules per asymmetric unit which differ mainly in the out-of-plant twist of one of the nitro groups (average twist of 11.1° in molecule a and only 4.2° in molecule b. The second nitro group is perpendicular to the ethylene plane in both molecules a and b. The twists for the nitro groups destroy any possible symmetry in the molecules. The reason for the departure from symmetry is presumably the close repulsive contacts between the iodine atoms and the oxygen atoms. The I to O approaches of the conjugated nitro group in 1 of 3.05 to 3.06 Å (intramolecular) and 3.03 to 3.20 Å (intermolecular) are significantly less than the normal van der Waals contact distances of 3.55 Å.[7] This intermolecular deficit is so large that it might be considered the iodo equivalent of a H bond, with the iodines acting as electron acceptors, and the nitro groups acting as lone

Table I. Reaction of Amines with 1,1-Diiododinitroethylene

amine	product	mp (°C)	yield (%)
$(CH_3)_2NH$	 2	218–219	68
$PrNH_2$	 3	209–211	64
$C_6H_5NH_2$	 4	182–183	68
	 5	249–250	66
$NH_2(CH_2)_2NH_2$	 6	261–262	74
$NH_2(CH_2)_3NH_2$	 7	243–244	60
$NH_2(CH_2)_4NH_2$	 8	211–212	91
$C(CH_2NH_2)_4$	 9	217–218	92

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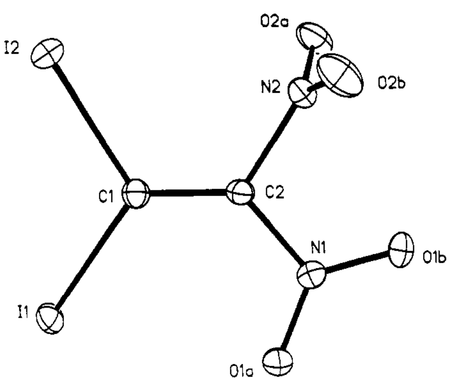

Figure 1. X-ray structure of 1,1-diiododinitroethylene (1).

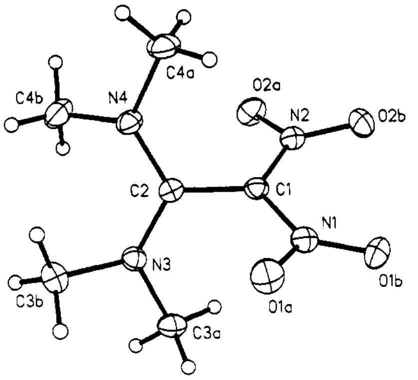

Figure 2. X-ray structure of 1,1-bis(dimethylamino)-2,2-dinitroethylene (2).

pair electron donors in an intermolecular charge-transfer interaction.

Displacement Reactions. Few *gem*-dinitro olefins have been reported, and stable examples generally have substituents capable of supporting a positive charge adjacent to the dinitro groups.[8] Products derived from 1,1-dinitroethylene as an unstable reaction intermediate have been obtained.[9] Vicinal halo nitro olefins are susceptible to Michael additions and substitutions by nucleophiles.[10] Therefore, some reactions of 1 with nucleophiles were examined as a potential source of new dinitro olefin derivatives.

Amines reacted rapidly with 1 at 0 °C in methylene chloride to give stable, high-melting substitution products, shown in Table I. Good to excellent yields of the substitution products of both iodines were obtained from secondary as well as primary aliphatic amines and anilines. Dimethylamine, propylamine, and aniline gave, respectively, 1,1-bis(dimethylamino)-2,2-dinitroethylene (2), 1,1-bis(*n*-propylamino)-2,2-dinitroethylene (3), and 1,1-bis(phenylamino)-2,2-dinitroethylene (4). Diamines gave cyclic products, with no evidence of the polymeric materials that would be obtained if amino groups of separate diamine molecules were to react with 1. Thus, *o*-phenylenediamine, ethylenediamine, 1,3-diaminopropane, and 1,4-diaminobutane gave 2-(dinitromethylene)benzimidazole (5), 2-(dinitromethylene)-1,3-diazacyclopentane (6), 2-(dinitromethylene)-1,3-diazacyclohexane (7), and 2-(dinitromethylene)-1,3-diazacycloheptane (8), respectively. The tetramine, tetrakis(aminomethyl)methane, gave the spiro substitution product 3,9-bis(dinitromethylene)-2,4,8,10-tetraazaspiro[5.5]undecane (9) in 92% yield, a noteworthy yield for a four-center substitution reaction. The high melting points of the products are consistent with dipolar structures, as would be expected for the effect of two electron-withdrawing nitro groups and two electron-supplying amino substituents on the double bond.

By analogy to the reactions of other amines with 1, ammonia would be expected to give 1,1-diamino-2,2-dinitroethylene. The sole product, however, was found to be ammonium cyanodinitromethide. This salt, formed in 95% yield based on UV analysis,[11] was isolated as the potassium salt in 74% yield. The reaction can be visualized on the basis of loss of HI from the monosubstitution product or of loss of ammonia from the disubstitution product.

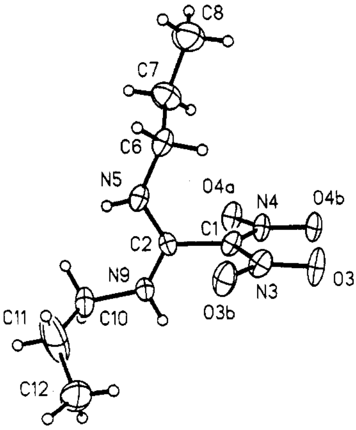

Figure 3. X-ray structure of 1,1-bis(*n*-propylamino)-2,2-dinitroethylene (3) showing one of the two disordered positions for C11 and C12.

$$I_2C{=}C(NO_2)_2 + NH_3 \rightarrow NH_4^{+}\,{}^{-}(NO_2)_2CCN$$

Addition of 1 to a solution of phenol in aqueous sodium hydroxide gave a 55% yield of 1,1-dinitro-2,2,2-triphenoxyethane. Analogous triphenoxy derivatives have been reported from reactions of phenoxide ion with 1,1-dichloro-2-nitroethylene and 1,1,2-trichloro-2-nitroethylene.[12]

$$PhOH + I_2C{=}C(NO_2)_2 \xrightarrow{NaOH} (PhO)_3CCH(NO_2)_2$$

Another nucleophile that was examined for reactivity with 1 is nitrite ion. An excess of potassium nitrite gave the dipotassium salt of tetranitroethane in 90% yield. The same salt has been obtained from 1,1,1-trinitrochloroethane and potassium nitrite.[13]

$$I_2C{=}C(NO_2)_2 + KNO_2 \rightarrow KO_2N{=}C(NO_2)C(NO_2){=}NO_2K$$

Structure of 1,1-Diaminoethylenes. 1-Amino-2-nitroethylenes, as well as 1,1-diamino-2-nitroethylenes,[14] have been shown by UV and IR spectroscopy to possess dipolar structures. The barrier to rotation of push–pull ethylenes depends on the degree of charge separation, and

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Table II. Bond Distances and Angles

		bond distances					bond angles	
no.	TWIST[a]	C=C	C—NO_2a	C—NO_2b	C—am1	C—am2	NCN(nit)	NCN(am)
1a[b]	0.1	1.331 (10)	1.454 (10)	1.494 (10)			109.4 (6)	
1b	1.8	1.334 (11)	1.444 (12)	1.473 (11)			108.9 (7)	
2	51.4	1.434 (3)	1.395 (2)	1.400 (3)	1.330 (3)	1.339 (2)	119.8 (2)	119.6 (2)
3	86.9	1.475 (13)	1.405 (14)	1.386 (11)	1.301 (15)	1.282 (13)	122.2 (9)	124.3 (9)
4	71.4	1.451 (11)	1.399 (11)	1.324 (10)	1.322 (11)	1.338 (11)	123.4 (6)	117.6 (6)
6a[b]	2.0	1.430 (5)	1.415 (5)	1.404 (5)	1.322 (5)	1.321 (5)	117.9 (3)	110.4 (3)
6b	0.6	1.439 (5)	1.414 (5)	1.395 (5)	1.326 (5)	1.328 (5)	118.2 (3)	109.8 (3)
7	89.0	1.473 (4)	1.383 (2)	1.383 (2)	1.297 (4)	1.306 (4)	123.8 (2)	121.6 (3)
8	79.3	1.473 (3)	1.377 (3)	1.376 (3)	1.315 (3)	1.307 (3)	118.5 (2)	124.4 (2)
9a[c]	85.1	1.474 (5)	1.361 (5)	1.377 (6)	1.297 (5)	1.324 (5)	124.0 (3)	121.3 (3)
9b(1)	68.6	1.465 (5)	1.388 (5)	1.381 (6)	1.318 (5)	1.316 (5)	121.8 (3)	121.0 (3)
9b(2)	74.5	1.475 (6)	1.378 (6)	1.372 (5)	1.312 (5)	1.307 (5)	123.4 (4)	121.8 (4)

[a] TWIST is defined as the angle between the bisectors of the 1,1- and the 2,2-substituent angles[24] on a Newman diagram (i.e., a projection down the C=C bond) of the olefin; this quantity uniquely defines the "average twist" even when the two olefin carbons are bowed (pyramidalized) as well as twisted. Initial values deduced from the diagram are reduced by 180° if greater than 90°, and the absolute value is taken; thus, final values lie between 0 and 90.0°. Esd's for twist angles are of the same order of magnitude as those listed for the bond angles. [b] Two molecules in the asymmetric unit. [c] Two crystal forms: **9a** is an acetonitrile solvate, with $^1/_2$ molecule (1 olefin) per asymmetric unit; **9b** is a DMSO solvate, with 1 molecule (2 independent olefins) per asymmetric unit.

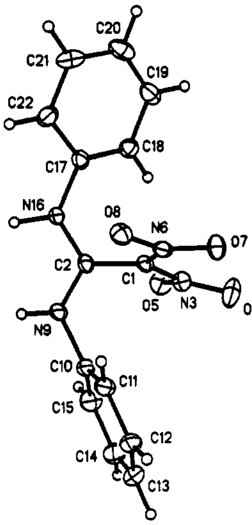

Figure 4. X-ray structure of 1,1-bis(phenylamino)-2,2-dinitroethylene (**4**).

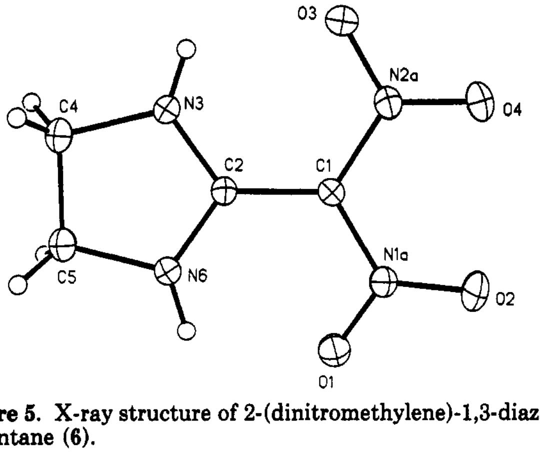

Figure 5. X-ray structure of 2-(dinitromethylene)-1,3-diazacyclopentane (**6**).

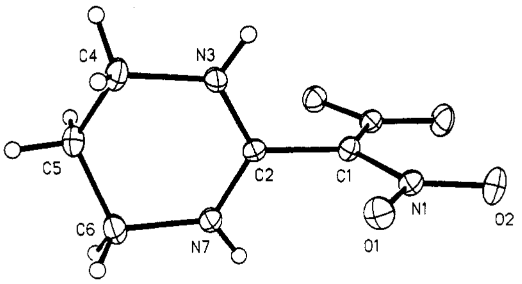

Figure 6. X-ray structure of 2-(dinitromethylene)-1,3-diazacyclohexane (**7**) showing one of the two disordered positions for C5.

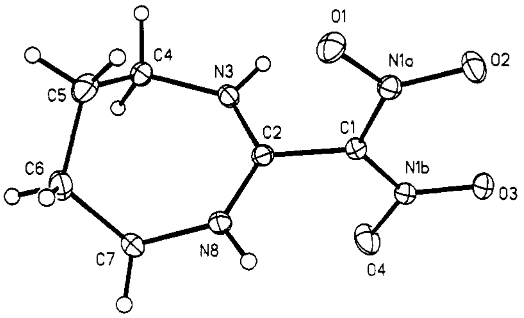

Figure 7. X-ray structure of 2-(dinitromethylene)-1,3-diazacycloheptane (**8**).

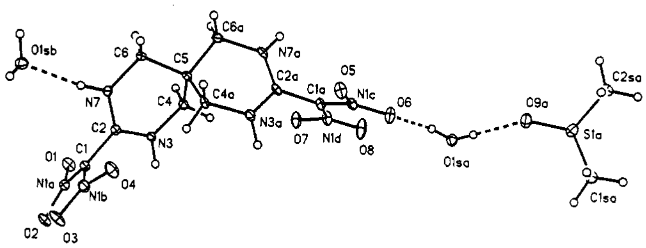

Figure 8. X-ray structure of 3,9-bis(dinitromethylene)-2,4,8,10-tetraazaspiro[5.5]undecane (**9**) showing the hydrogen-bonded interactions with the included solvent molecules.

steric interaction of substituents can result in permanently twisted olefins.[15] X-ray crystallographic studies[15c] of twisted push-pull ethylenes have shown that the C=C bond lengths are greater than those of normal olefins and the C—N bond lengths in the donor parts of the molecules are shorter than N—C(sp^2) bonds. The most twisted push-pull ethylene reported previously is 1,3-dibenzyl-2-(4,4-dimethyl-2,5-dithioxocyclohexylidene)imidazolidine, with a twist angle of 80.8°,[16] which contains a diamine

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[15] (a) Wennerbeck, I.; Sandstrom, J. *Org. Magn. Reson.* **1972**, *4*, 783. (b) Kalinowski, H. O.; Kessler, H. *Topics in Stereochemistry* Interscience: New York, 1973; Vol. 7, p 295. (c) Sandstrom, J. *Top. Stereochem.* **1983**, *14*, 83. (d) Sandstrom, J.; Sjostrand, U.; Wennerbeck, I. *J. Am. Chem. Soc.* **1977**, *99*, 4526. (e) Sandstrom, J.; Sjostrand, U. *Tetrahedron* **1978**, *34*, 371.

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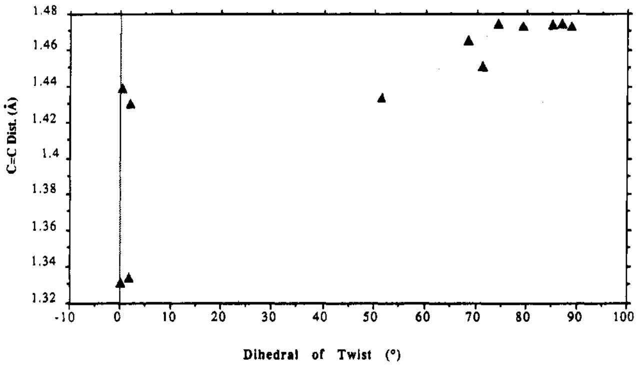

Figure 9. Olefin bond lengths vs twist angle.

donor and a dithiolane acceptor at each end of the twisted olefin.

Structures of the corresponding push–pull olefins which have two amine donors and two nitro acceptors have not yet been reported. X-ray structures of seven of the compounds listed in Table I (compounds **2–4**, **6–9**) are depicted in Figures 2–8. The compounds exhibit, with one exception, large "permanent" or ground-state twists in their crystals, ranging from 51.4 to 89.0° in magnitude, with concomitant bond-distance distortions, as shown in Table II. The single exception is molecule **6**, formed by the reaction of ethylenediamine with **1**. This molecule shows the same pronounced olefin distance lengthening (C1=C2 is 1.435 Å, average of two molecules) as others in the series, but is essentially planar. This planarity is reinforced by two intramolecular H bonds which form between the amino N–H and the nitro O–N bonds, but the same opportunity for H bonding exists in the highly twisted 6- and 7-membered ring analogues (compounds **7** and **8**). The planarity of the 5-membered ring compound may be due to reduced crowding that would favor twisting, or more favorable hydrogen bonding or intermolecular packing effects. A number of mononitro enamine structures have been reported with similar central-bond length increases, but with little or no twist,[17] in at least one case stabilized by an intramolecular H bond formed between the amine and a nitro oxygen atom.[18] The mononitro analogue of **2** [1,1-bis(dimethylamino)-2-nitroethylene], which is somewhat crowded, has a central twist of ca. 33°.[19]

The central olefin bond distances and twists, for all of the crystal structures reported herein, are shown in Figure 9. In the region of high twist values, the points cluster together, while in the low twist region there is wide scatter. This can be interpreted to mean that large twists always indicate a strong contribution of dipolar diene forms, but the converse is not necessarily true; i.e., a polarized olefin only twists if it is destabilized by steric interference. Figure 10 illustrates the expected approximate inverse correlation between the central, formally double, and outer, formally single, olefin bond distances.

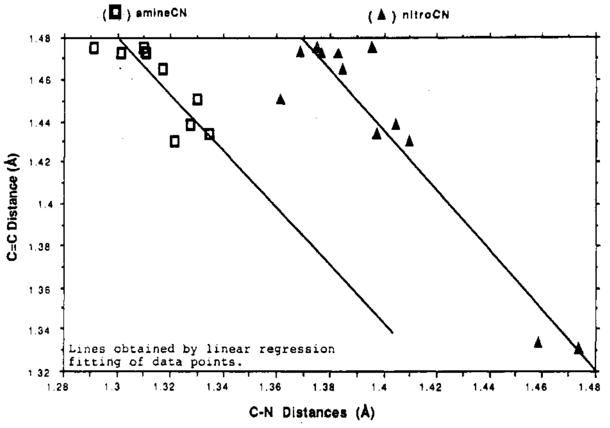

Figure 10. Correlation of olefin bond lengths.

Improved Preparation of 1. In the original preparation,[6] the nitration of tetraiodoethylene with red fuming nitric acid at 100 °C for 15 min gave **1** in 0–25% yield, along with triiodonitroethylene in 40–70% yield. We found the yield to be sensitive to reaction temperature, time, and particle size of the tetraiodoethylene. Thus, reducing the temperature to 90 °C and using finely ground tetraiodoethylene improved the yield to 41%. Similar results were obtained using the more readily available 90% "white fuming" nitric acid in place of the red fuming acid. Yields of 60–65% were obtained using 90% nitric acid at 70 °C, with a 15-min reaction time. Lower yields were obtained with 80% and with 95% acid. Extending the reaction time from 15 to 30 min reduced the yields to 0–5%.

Experimental Section

NMR spectra were obtained using a Varian T-60 or a Bruker AC 200 MHz spectrometer. Infrared spectra were recorded with a Perkin-Elmer 700 spectrophotometer. UV spectra were recorded with a Beckman DK-1A spectrophotometer. Melting points were determined in open capillary tubes with an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were carried out by Gailbraith Laboratories, Inc., Knoxville, TN. Polynitro compounds are potentially explosive and proper shielding should be used.

1,1-Diiododinitroethylene (1). Finely ground tetraiodoethylene (80.0 g, 0.15 mol) was added over a 10-min period, with vigorous stirring, to 300 mL of 90% HNO_3; the temperature rose to 40 °C. After the solution was stirred at 40 °C for 5 min, it was heated quickly to 70 °C. After 15 min, the dark red, heterogeneous mixture was poured onto 1 L of ice. The resulting black solid was dissolved in 250 mL of CH_2Cl_2 and washed with H_2SO_3 (100 mL), water (3 × 100 mL), and brine (100 mL) and dried ($MgSO_4$). Removal of solvent gave 35.8 g (65%) of a yellow solid, mp 65–67 °C. Recrystallization from CH_2Cl_2/hexane gave yellow needles, mp 68–69 °C (lit.[8] mp 68–69 °C): IR (KBr) 1520, 1360, 1320 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 24.8, 157.3.

1,1-Bis(dimethylamino)-2,2-dinitroethylene. A solution of dimethylamine (1.0 g, 22.2 mmol) in CH_2Cl_2 (10 mL) was added dropwise, at 0 °C, to a solution of 1,1-diiododinitroethylene (**1**) (2.0 g, 5.40 mmol) in CH_2Cl_2 (30 mL). The yellow solution was stirred at 0 °C for 1 h, and a solid precipitated. The solution was then washed with water (2 × 100 mL) and brine (50 mL) and dried ($MgSO_4$). Solvent was removed in vacuo to afford 0.8 g (68%) of 1,1-bis(dimethylamino)-2,2-dinitroethylene, a bright yellow solid. An analytical sample was recrystallized from $CHCl_3$/hexanes: mp 218–219 °C dec; IR (KBr) 2970, 1605, 1500, 1420, 1280, 1140, 1090, 900, 810 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 264 (9260), 302 (2730), 340 (11 000); ^1H NMR ($CDCl_3$) δ 3.07 (s, 6 H), 3.20 (s, 6 H); ^{13}C NMR (DMSO-d_6) δ 40.83, 42.38, 128.20, 162.31. Anal. Calcd for $C_6H_{12}N_4O_4$: C, 35.15; H, 5.92; N, 27.44. Found: C, 35.15; H, 5.98; N, 27.14.

1,1-Bis(*n*-propylamino)-2,2-dinitroethylene. By the above procedure, 1,1-diiododinitroethylene (2.0 g, 5.40 mmol) was treated with *n*-propylamine (1.3 g 21.60 mmol) to give a product insoluble in CH_2Cl_2. The material was washed with water and ether to give 1,1-bis(*n*-propylamino)-2,2-dinitroethylene (0.8 g, 64%), a white solid, mp 209–211 °C dec: IR (KBr) 3320, 3300, 1640, 1560, 1480, 1250, 1140 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 346 (16 000); ^1H NMR (DMSO-d_6) δ 0.80 (t, J = 7 Hz, 3 H), 0.91 (t, J = 7 Hz, 3 H),

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1.39–1.61 (m, 4 H), 3.03 (t, J = 7 Hz, 2 H), 3.24 (t, J = 7 Hz, 2 H), 8.97 (br, 1 H), 9.78 (br, 1 H); ^{13}C NMR (DMSO-d_6) δ 10.95, 11.10, 20.37, 21.90, 43.86, 46.09, 124.72, 156.06. Anal. Calcd for $C_8H_{16}N_4O_4$: C, 41.37; H, 6.94; N, 24.12. Found: C, 41.39; H, 7.04; N, 23.85.

1,1-Bis(phenylamino)-2,2-dinitroethylene. The reaction of 1,1-diiododinitroethylene (2.0 g, 5.40 mmol) with aniline (2.0 g, 21.62 mmol) by the above procedure gave 1,1-bis(phenylamino)-2,2-dinitroethylene (1.1 g, 68%), a yellow solid. An analytical sample was recrystallized from acetone: mp 182–183 °C dec; IR (KBr) 3300, 3110, 1620, 1580, 1500, 1280, 1140, 780 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 270 (13 500), 297 (13 100), 248 (14 000); ^{1}H NMR (DMSO-d_6) δ 7.34–7.49 (m, 10 H), 11.82 (br, 2 H); ^{13}C NMR (DMSO-d_6) δ 123.24, 126.98, 127.73, 129.52, 135.80, 155.07. Anal. Calcd for $C_{14}H_{12}N_4O_4$: C, 56.00; H, 4.03; N, 18.66. Found: C, 55.70; H, 3.92; H, 18.58.

2-(Dinitromethylene)benzimidazole. By the above method, the reaction of 1,1-diiododinitroethylene (2.0 g, 5.40 mmol) with o-phenylenediamine (0.6, 5.40 mmol) and triethylamine (1.1 g, 10.8 mmol) gave 2-(dinitromethylene)benzimidazole (0.8 g, 66%), a green solid. An analytical sample recrystallized from tetrahydrofuran: mp 249–250 °C dec: IR (KBr) 3360, 1560, 1500, 1320, 1280, 1250, 1140, 780 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 240 (1100), 320 (19 300), 335 (21 100); ^{1}H NMR (DMSO-d_6) δ 7.37–7.36 (m, 2 H), 7.70–7.76 (m, 2 H), 13.00 (br, 2 H); ^{13}C NMR (DMSO-d_6) δ 113.49, 124.85, 129.34, 130.23, 141.18. Anal. Calcd for $C_8H_6N_4O_4$: C, 43.25; H, 2.72; N, 25.22. Found: C, 43.09; H, 2.71; N, 24.82.

2-(Dinitromethylene)-1,3-diazacyclopentane. The reaction of 1,1-diiododinitroethylene (2.0 g, 5.40 mmol) with ethylenediamine (5.0 g, 83 mmol) by the above procedure gave 2-(dinitromethylene)-1,3-diazacyclopentane, a yellow solid (0.7 g, 74%). An analytical sample was recrystallized from $CHCl_3$/hexanes: mp 261–262 °C dec; IR (KBr) 3410, 2950, 1565, 1500, 1290, 1200, 1115, 1050, 1005, 825, 790, 780 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 280 (14 100), 295 (6750), 330 (6840); ^{1}H NMR (DMSO-d_6) δ 3.75 (s, 4 H), 8.86 (br, 2 H); ^{13}C NMR (DMSO-d_6) δ 43.88, 129.75, 155.23. Anal. Calcd for $C_4H_6N_4O_4$: C, 27.59; H, 3.47; N, 32.18. Found: C, 27.70; H, 3.47; N, 32.19.

2-(Dinitromethylene)-1,3-diazacyclohexane. The reaction of 1,1-diiododinitroethylene (2.0 g, 5.40 mmol), 1,3-diaminopropane (1.6 g, 21.52 mmol), and triethylamine (2.2 g, 21.52 mmol) by the above method gave 2-(dinitromethylene)-1,3-diazacyclohexane (0.6 g, 60%), a white solid, mp 240–242 °C. An analytical sample was obtained by recrystallization from acetone/hexanes: mp 243–244 °C dec; IR (KBr) 3350, 1680, 1615, 1500, 1460, 1300, 1280 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.71–2.76 (m, 2 H), 4.27–4.32 (m, 4 H), 10.53 (br, 2 H); ^{13}C NMR (DMSO-d_6) δ 17.31, 38.68, 126.83, 153.61. Anal. Calcd for $C_5H_8N_4O_4$: C, 31.92; H, 4.29; N, 29.78. Found: C, 32.14; H, 4.36; N, 29.71.

2-(Dinitromethylene)-1,3-diazacycloheptane. The reaction of 1,1-diiododinitroethylene (2.0 g, 5.40 mmol) with 1,4-diaminobutane (1.0 g, 11.36 mmol) and triethylamine (3.0 g, 29.70 mmol) by the above method gave 0.6 g of yellow solid. The mother liquor was washed with 10% HCl (30 mL), water (3 × 50 mL), and brine (50 mL) and dried ($MgSO_4$). Evaporation of solvent gave a yellow oil which was triturated with acetone/hexanes to give 0.4 g of yellow solid. The total yield of 2-(dinitromethylene)-1,3-diazacycloheptane was 1.0 g (91%), mp 205–209 °C. An analytical sample was obtained by recrystallization from acetone/hexanes/ether: mp 211–212 °C; IR (KBr) 3260, 3150, 1620, 1500, 1260, 1210, 1140 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.79 (s, 4 H), 3.38 (s, 4 H), 8.31 (br, 2 H); ^{13}C NMR (DMSO-d_6) δ 25.87, 44.56, 128.29, 159.28. Anal. Calcd for $C_6H_{10}N_4O_4$: C, 35.65; H, 4.98; N, 27.71. Found: C, 35.95; H, 4.85; N, 27.60.

3,9-Bis(dinitromethylene)-2,4,8,10-tetraazaspiro[5.5]undecane. A solution of tetrakis(aminomethyl)methane hydrogensulfate salt[20] (2.66 g, 8.11 mmol) and triethylamine (6.55 g, 64.88 mmol) in 50 mL of 60% aqueous methanol was cooled to 0 °C, and a solution of 1,1-diiododinitroethylene (6 g, 16.22 mmol) in 40 mL of 60% aqueous methanol was added dropwise over 15 min. The orange solution was stirred at 0 °C for 1 h during which time a solid precipitated. The solid was filtered and washed with water (2 × 50 mL) and Et_2O (2 × 50 mL) to afford 2.4 g of a yellow solid. The mother liquor was cooled at −10 °C overnight to give another 0.3 g of 3,9-bis(dinitromethylene)-2,4,8,10-tetraazaspiro[5.5]undecane (92%), mp 211 °C dec. An analytical sample was recrystallized from acetone: mp 217–218 °C dec; IR (KBr) 3350, 1610, 1500, 1360, 1260, 1120 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 3.46 (s, 8 H), 10.45 (s, 4 H); ^{13}C NMR (DMSO-d_6) δ 24.56, 43.25, 125.91, 153.65. Anal. Calcd for $C_9H_{12}O_8N_8$: C, 30.01; H, 3.36; N, 31.10. Found: C, 30.28; H, 3.33; N, 31.39.

Potassium Dinitrocyanomethide. Ammonia was bubbled through a solution of 1,1-diiododinitroethylene (1.0 g, 2.7 mmol) in dichloromethane (10 mL) at −20 °C until precipitation of yellow solid ceased (about 30 s). The precipitate was filtered and dissolved in a minimum amount of water. A saturated solution of potassium chloride was added dropwise until further addition failed to produce a precipitate. The mixture was filtered, and the filtrate was concentrated to dryness under vacuum. The above procedure was repeated with the residue to give a total of 0.4 g (74%) of potassium dinitrocyanomethide, mp 265–270 °C dec (lit.[21] mp 262–264 °C dec). A mixed mp showed no depression.

In another experiment, ammonia was passed through a 4.51 × 10^{-4} M solution of 1,1-diiododinitroethylene in tetrahydrofuran. Saturated aqueous thiosulfate solution was added to remove interference from I_2. The mixture was then diluted to 4.3 × 10^{-5} M with tetrahydrofuran and analyzed at 345 nm. Using the known extinction coefficient, the conversion of 2 to 12 was 95%.

1,1-Dinitro-2,2,2-triphenoxyethane (18). To a solution of phenol (2.75 mg, 2.92 mmol) and sodium hydroxide (117 mg, mmol) in water (5 mL) was added, with stirring, 1,1-diiododinitroethylene (540 mg, 1.56 mmol). After 5 min, the mixture became homogeneous and then solid the precipitated. The product was extracted with ether (10 mL), the organic layer was dried ($MgSO_4$), and ether was evaporated to give 1,1-dinitro-2,2,2-triphenoxyethane (320 mg, 55%). An analytically pure sample was obtained by recrystallization from benzene/hexanes: mp 95–98 °C; IR (CH_2Cl_2) 3100, 1580, 1490, 1200, 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.00 (m). Anal. Calcd for $C_{20}H_{16}N_2O_7$: C, 60.61; H, 4.07; N, 7.07. Found: C, 60.52; H, 3.98; N, 6.85.

Dipotassium Tetranitroethane. A solution of 1,1-diiododinitroethylene (1.0 g, 2 mmol) in 8 mL of 60% aqueous methanol was added dropwise to a solution of KNO_2 (2.0 g, 24 mmol) in 8 mL of 60% aqueous methanol. The yellow solution immediately became dark red and a yellow solid precipitated. The product was filtered after 18 h and washed with methanol to give dipotassium tetranitroethane (0.7 g, 90%), a bright yellow solid: mp 280 °C (exp) (lit. mp 275 °C dec,[22] 293–294 °C dec.).[13] The IR spectrum was identical to that of an authentic sample.

X-ray Analysis. Data collection for all compounds was done on an automated Siemens R3m/V diffractometer equipped with an incident beam monochromator using the $\theta/2\theta$ scan mode, with scan width $[2\theta(K_{\alpha 1})-1.0]$ to $[2\theta(K_{\alpha 2})+1.0]°$ and an ω scan rate which varied as a function of count rate. All data sets were corrected for Lorentz and polarization effects and unless noted no absorption corrections were applied. All structures were solved by direct methods and refined by full-matrix least-squares method with the aid of the SHELXTL system of programs.[23] Specific experimental details for each compound follow.

X-ray analysis of 1,1-diiododinitroethylene (1): $C_2N_2O_4I_2$, FW = 369.8; triclinic space group $P\bar{1}$; a = 8.023 (1), b = 8.108 (1), and c = 12.781 (2) Å; α = 100.61 (1), β = 101.38 (2), and γ = 91.58 (1)°; V = 799.4 (2) Å^3; Z = 4; ρ_{calc} = 3.073 mg mm^{-3}; λ(Mo Kα) = 0.710 73 Å; μ = 7.75 mm^{-1}; F(000) = 656; T = 203 K.

A clear yellow 0.04 × 0.20 × 0.24 mm crystal, in the shape of a plate, was used for data collection. Lattice parameters were determined from 25 centered reflections within $20 \le 2\theta \le 30°$. The data collection range of hkl was $-11 \le h \le 11$, $0 \le k \le 11$, $-18 \le l \le 17$, with $[(\sin\theta)/\lambda]_{max}$ = 0.70. Three standards, mon-

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itored after every 97 reflections, exhibited random variations with deviations up to ±2.0% during the data collection. A set of 3587 reflections was collected with an ω scan rate varying from 3.0 to 15.0 deg/min. There were 3363 unique reflections, and 2765 were observed with $F_o > 3\sigma(F_o)$. Empirical absorption corrections were applied (maximum and minimum transmission factors are 0.98 and 0.35, respectively). The refinement varied 182 parameters: atom coordinates and anisotropic thermal parameters for all atoms. Final residuals were $R = 0.040$ and $R_w = 0.045$ with final difference Fourier excursions of 1.89 and −1.46 e Å^{-3} (all strong ripples in the final difference Fourier were within 1 Å of the various iodine atoms).

X-ray analysis of 1,1-bis(dimethylamino)-2,2-dinitroethylene (2): $C_6H_{12}N_4O_4$, FW = 204.2; monoclinic space group $P2_1/n$; $a = 7.201$ (7), $b = 17.32$ (2), and $c = 8.122$ (8) Å; $\beta = 108.54$ (6)°; $V = 960.6$ (2) Å^3; $Z = 4$; $\rho_{calc} = 1.412$ mg mm^{-3}; λ(Cu Kα) = 1.541 84 Å; $\mu = 0.98$ mm^{-1}; $F(000) = 432$; $T = 295$ K.

A yellow 0.42 × 0.38 × 0.35 mm crystal, in the shape of a prism, was used for data collection. Lattice parameters were determined from 25 centered reflections within $55.5 \leq 2\theta \leq 85.3°$. The data collection range of *hkl* was $0 \leq h \leq 7$, $0 \leq k \leq 18$, $-8 \leq l \leq 8$, with $[(\sin\theta/\lambda]_{max} = 0.54$. Three standards, monitored after every 60 reflections, exhibited random variations with deviations up to ±2.0% during the data collection. A set of 1455 reflections were collected with an ω scan rate varying from 4.00 to 15.0 deg/min. There were 1278 unique reflections, and 1213 were observed with $F_o \geq 3\sigma(F_o)$. The refinement varied 140 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms, H atoms included using riding model [coordinate shifts of C applied to attached H atoms, C–H distance set to 0.96 Å, H angles idealized]. Final residuals were $R = 0.038$ and $R_w = 0.055$ with final difference Fourier excursions of 0.14 and −0.16 e Å^{-3}.

X-ray analysis of 1,1-bis(*n*-propylamino)-2,2-dinitroethylene (3): $C_8H_{16}N_4O_4$, FW = 232.2; triclinic space group $P\bar{1}$; $a = 6.800$ (3), $b = 9.286$ (3), and $c = 10.155$ (3) Å; $\alpha = 93.51$ (2), $\beta = 96.61$ (2), and $\gamma = 107.33$ (3)°; $V = 604.9$ (4) Å^3, $Z = 2$; $\rho_{calc} = 1.275$ mg mm^{-3}; λ(Cu Kα) = 1.541 84 Å; $\mu = 0.83$ mm^{-1}; $F(000) = 248$, $T = 295$ K.

A clear colorless 0.10 × 0.22 × 0.65 mm crystal, in the shape of a rectangular prism, was used for data collection. Lattice parameters were determined from 25 centered reflections within $23 \leq 2\theta \leq 47°$. The data collection range of *hkl* was $-7 \leq h \leq 6$, $-10 \leq k \leq 10$, $-11 \leq l \leq 2$, with $[(\sin\theta)/\lambda]_{max} = 0.56$. Three standards, monitored after every 97 reflections, exhibited random variations with deviations up to ±5.0% during the data collection. A set of 1906 reflections was collected using an ω scan rate varying from 8.0 to 30.0 deg/min. There were 1561 unique reflections, and 906 were observed with $F_o > 3\sigma(F_o)$. The refinement varied 161 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms, coordinates for the hydrogen atoms bonded to nitrogen atoms. All other H atoms included using riding model [coordinate shifts of C applied to attached H atoms, C–H distance set to 0.96 Å, H angles idealized]. C–C distances in the disordered side chain restrained to be equal. Final residuals were $R = 0.102$ and $R_w = 0.104$ with final difference Fourier excursions of 0.44 and −0.41 e Å^{-3}.

X-ray analysis of 1,1-bis(phenylamino)-2,2-dinitroethylene (4): $C_{14}H_{12}N_4O_4$, FW = 300.3; monoclinic space group $P2_1/c$; $a = 10.557$ (5), $b = 10.475$ (5), and $c = 12.857$ (6) Å; $\beta = 91.37$ (4); $V = 1421$ (1) Å^3; $Z = 4$; $\rho_{calc} = 1.40$ mg mm^{-3}; λ(Mo Kα) = 0.710 73 Å; $\mu = 0.10$ mm^{-1}; $F(000) = 624$, $T = 295$ K.

A clear colorless 0.05 × 0.38 × 0.50 mm crystal, in the shape of a plate, was used for data collections. Lattice parameters were determined from 25 centered reflections within $18 \leq 2\theta \leq 25°$. The data collection range of *hkl* was $-11 \leq h \leq 11$, $0 \leq k \leq 11$, $0 \leq l \leq 13$, with $[(\sin\theta)/\lambda]_{max} = 0.54$. Three standards, monitored after every 97 reflections, exhibited random variations with deviations up to ±2.0% during the data collection. A set of 2092 reflections was collected using an ω scan rate varying from 3.0 to 15.0 deg/min. There were 1861 unique reflections, and 1311 were observed with $F_o > 3\sigma(F_o)$. The refinement varied 218 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms; coordinates for H atoms bonded to nitrogen atoms and isotropic thermal parameters for all hydrogen atoms. Remaining H atoms included using riding model [coordinate shifts of C applied to attached H atoms, C–H distance set to 0.96 Å, H angles idealized]. Final residuals were $R = 0.077$ and $R_w = 0.074$ with final difference Fourier excursions of 0.36 and −0.30 e Å^{-3}.

X-ray analysis of 2-(dinitromethylene)-1,3-diazacyclopentane (6): $C_4H_6N_4O_4$, FW = 174.1; monoclinic space group $P2_1/a$; $a = 6.687$ (1), $b = 23.695$ (4), and $c = 8.584$ (1) Å; $\beta = 92.39$ (1)°; $V = 1359.0$ (4) Å^3; $Z = 8$; $\rho_{calc} = 1.70$ mg mm^{-3}; λ(Cu Kα) = 1.541 84 Å; $\mu = 1.282$ mm^{-1}; $F(000) = 720$, $T = 295$ K.

A clear colorless 0.10 × 0.10 × 0.42 mm crystal, in the shape of a rod, was used for data collection. Lattice parameters were determined from 25 centered reflections within $42.1 \leq 2\theta \leq 58.7°$. The data collection range of *hkl* was $-7 \leq h \leq 0$, $0 \leq k \leq 25$, $-9 \leq l \leq 9$, with $[(\sin\theta)/\lambda]_{max} = 0.54$. Three standards, monitored after every 97 reflections, exhibited random variation with deviations up to ±3.0% during the data collection. A set of 2110 reflections was collected using an ω scan rate varying from 5.0 to 30.0 deg/min. There were 1858 unique reflections, and 1439 were observed with $F_o > 3\sigma(F_o)$. The refinement varied 230 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms, and coordinates for the hydrogen atoms bonded to nitrogen atoms. All other H atoms included using riding model [coordinate shifts of C applied to attached H atoms, C–H distance set to 0.96 Å, H angles idealized]. Final residuals were $R = 0.055$ and $R_w = 0.058$ with final difference Fourier excursions of 0.27 and −0.24 e Å^{-3}.

X-ray analysis of 2-(dinitromethylene)-1,3-diazacyclohexane (7): $C_5H_8N_4O_4$, FW = 188.2; orthorhombic space group $Pnma$; $a = 7.530$ (1), $b = 7.999$ (1), and $c = 12.454$ (2) Å; $V = 750.1$ (2) Å^3; $Z = 4$ ($^1/_2$ molecule per asymmetric unit); $\rho_{calc} = 1.666$ mg mm^{-3}; λ(Cu Kα) = 1.541 84 Å; $\mu = 1.207$ mm^{-1}; $F(000) = 392$; $T = 295$ K.

A clear colorless 0.32 × 0.34 × 0.08 mm crystal, in the shape of a plate, was used for data collection. Lattice parameters were determined from 25 centered reflections within $35.6 \leq 2\theta \leq 44.3°$. The data collection range of *hkl* was $0 \leq h \leq 8$, $-8 \leq k \leq 0$, $0 \leq l \leq 13$, with $[(\sin\theta)/\lambda]_{max} = 0.55$. Three standards, monitored after every 97 reflections, exhibited random variations with deviations up to ±2.0% during the data collection. A set of 642 reflections was collected using an ω scan rate varying from 4.0 to 15.0 deg/min. Numerical absorption corrections were calculated by the Gaussian integration method after indexing the crystal faces and measuring the distance of each face from a common reference point inside the crystal. There were 559 unique reflections, and 516 were observed with $F_o > 3\sigma(F_o)$. The structure contained $^1/_2$ molecule per asymmetric unit such that C1–C2–N3–C4–C6 and N7 and lie in a mirror plane with the two NO_2 groups arranged symmetrically above and below the plane and C5 disordered above and below the plane in a 1:1 ratio. The refinement varied 78 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms, and coordinates for the hydrogen atoms bonded to nitrogen atoms. All other H atoms included using riding model [coordinate shifts of C applied to attached H atoms, C–H distance set to 0.96 Å, H angles idealized]. Final residuals were $R = 0.035$ and $R_w = 0.051$ with final difference Fourier excursions of 0.29 and −0.18 e Å^{-3}.

X-ray analysis of 2-(dinitromethylene)-1,3-diazacycloheptane (8): $C_6H_{10}N_4O_4$, FW = 202.2; orthorhombic space group $Pbca$; $a = 9.207$ (2), $b = 10.439$ (3), and $c = 17.855$ (4) Å; $V = 1716.1$ (7) Å^3; $Z = 8$; $\rho_{calc} = 1.565$ mg mm^{-1}; λ(Mo Kα) = 0.710 73 Å; $\mu = 0.124$ mm^{-1}; $F(000) = 848$; $T = 295$ K.

A clear colorless 0.16 × 0.24 × 0.42 mm crystal, in the shape of a prism, was used for data collection. Lattice parameters were determined from 25 centered reflections within $23.2 \leq 2\theta \leq 27.7°$. The data collection range of *hkl* was $0 \leq h \leq 10$, $0 \leq k \leq 12$, $0 \leq l \leq 21$, with $[(\sin\theta)/\lambda]_{max} = 0.59$. Three standards, monitored after every 97 reflections, exhibited random variations with deviations up to ±2.5% during the data collection. A set of 1842 reflections was collected using an ω scan rate varying from 5.0 to 15.0 deg/min. There were 1526 unique reflections, and 1183 were observed with $F_o > 3\sigma(F_o)$. The refinement varied 158 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms, and coordinates for the hydrogen atoms. Final residuals were $R = 0.044$ and $R_w = 0.045$ with final difference Fourier excursions of 0.31 and −0.23 e Å^{-3}.

X-ray analysis of 3,9-bis(dinitromethylene)-2,4,8,10-tetraazaspiro[5.5]undecane (9): $C_9H_{12}N_8O_8{\cdot}(CH_3)_2SO{\cdot}H_2O$, FW = 456.4; orthorhombic space group $Pn2_1a$; $a = 10.888$ (3), $b =$

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11.478 (2), and c = 15.023 (4) Å; V = 1877.4 (8) Å^3; Z = 4; ρ_{calc} = 1.615 mg mm^{-3}; λ(Mo Kα) = 0.71073 Å; μ = 0.233 mm^{-1}; F(000) = 952; T = 233 K.

A yellow 0.15 × 0.26 × 0.57 mm crystal, in the shape of an irregular chunk, was used for data collection. Lattice parameters were determined from 30 centered reflections within $26.2 \leq 2\theta \leq 38.1°$. The data collection range of hkl was $0 \leq h \leq 12$, $0 \leq k \leq 13$, $0 \leq l \leq 17$, with $[(\sin\theta)/\lambda]_{max} = 0.59$. Three standards, monitored after every 97 reflections, exhibited random variations with deviations up to ±2.0% during the data collection. A set of 1923 reflections was collected using an ω scan rate varying from 4.0 to 20.0 deg/min. There were 1752 unique reflections, and 1568 were observed with $F_o > 3\sigma(F_o)$. The refinement varied 294 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms, and coordinates for the hydrogen atoms bonded to the nitrogen atoms and on the water molecule. All other H atoms included using riding model [coordinate shifts of C applied to attached H atoms, C–H distance set to 0.96 Å, H angles idealized]. Final residuals were R = 0.038 and R_w = 0.036 with final difference Fourier excursions of 0.24 and –0.32 e Å^{-3}.

X-ray analysis of molecule 9a: $C_9H_{12}N_8O_8 \cdot 2(CH_3CN)$, FW = 442.4; monoclinic space group $C2/c$; a = 14.281 (9), b = 9.077 (4), and c = 15.813 (9) Å; β = 115.41 (4)°; V = 1851 (2) Å^3; Z = 4 ($^1/_2$ molecule per asymmetric unit); ρ_{calc} = 1.587 mg mm^{-3}; λ(Mo Kα) = 0.71073 Å; μ = 0.125 mm^{-1}; F(000) = 920; T = 295 K.

A yellow 0.49 × 0.36 × 0.20 mm crystal, in the shape of an irregular prism (mounted in a capillary), was used for data collection. Lattice parameters were determined from 25 centered reflections within $19.0 \leq 2\theta \leq 34.7°$. The data collection range of hkl was $0 \leq h \leq 15$, $-9 \leq k \leq 0$, $-16 \leq l \leq 15$, with $[(\sin\theta)/\lambda]_{max} = 0.54$. Three standards, monitored after every 97 reflections, exhibited linear decay of ca. 10% during the data collection. A set of 1368 reflections was collected using a constant ω scan rate of 15.0 deg/min. There were 1213 unique reflections, and 966 were observed with $F_o > 3\sigma(F_o)$. The refinement varied 168 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms, and coordinates for the hydrogen atoms. Final residuals were R = 0.052 and R_w = 0.046 with final difference Fourier excursions of 0.24 and –0.29 e Å^{-3}.

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Registry No. **1**, 137143-78-3; **2**, 113110-14-8; **3**, 137143-79-4; **4**, 137143-80-7; **5**, 137143-81-8; **6**, 137143-82-9; **7**, 137143-83-0; **8**, 137143-84-1; **9**, 137143-85-2; **9**·$(CH_3)_2SO$, 137143-88-5; **9a**, 137143-89-6; $I_2C{=}CI_2$, 513-92-8; Me_2NH, 124-40-3; $PrNH_2$, 107-10-8; NH_2Ph, 62-53-3; $NH_2C_6H_4$-o-NH_2, 95-54-5; $(NH_2)_2C{=}CH_2$, 107-15-3; $NH_2(CH_2)_3NH_2$, 109-76-2; $NH_2(CH_2)_4NH_2$, 110-60-1; $(NH_2CH_2)_4 \cdot HSO_4$, 137143-87-4; NH_3, 7664-41-7; $(NO_2)_2CCN^- \cdot K^+$, 6928-22-9; PhOH, 108-95-2; $(NO_2)_2(C)_2(NO_2)_2 \cdot 2K$, 32607-31-1.

Supplementary Material Available: Tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters (35 pages). Ordering information is given on any current masthead page.

Prototropic Control of Organic Photochemistry. Hydrogen Bonding Effects on the Di-π-methane Photorearrangement

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The IR and UV spectra as well as the photochemistry of the isopropyl monoester of dibenzobarrelene dicarboxylic acid **2** were analyzed in detail in several media. A correlation was found between the photochemical results and the spectroscopically detected hydrogen-bonded structures of **2**. An equilibrium between dimeric (**2-HD**) and intramolecularly hydrogen bonded (**2-HI**) structures was detected by IR spectroscopy in nonpolar solvents having weak hydrogen-bond-accepting capabilities. The ratio of the two regioisomeric dibenzosemibullvalene products **3** and **4** formed in the di-π-methane photorearrangement of **2** was found to correlate with such an equilibrium, and it was concluded that intramolecular (**2-HI**) and dimeric (**2-HD**) hydrogen-bonded structures display significantly different photochemical reactivity. The infrared spectra and the photoproduct ratio in polar solvents possessing hydrogen-bond-accepting capabilities (e.g., acetonitrile), on the other hand, turned out to be concentration independent. High regioselectivity was found in the solid state where the dimer **2-HD** is the only species, leading to **4** as the major product. In contrast, **3** was obtained preferentially in aqueous sodium bicarbonate solutions where **2** exists as the carboxylate anion. Supporting evidence regarding the different hydrogen bonding arrangements in **2** was found in the solvent effects on its UV spectra.

1. Introduction

The effects of hydrogen bonding (HB) on the photophysical behavior of the excited states of organic compounds have been widely documented.[1] It has been shown that peculiar photobehavior induced by HB is largely dependent on structural factors. Intramolecular hydrogen bonding (IHB), for instance, may induce strongly shifted emission as in methyl salicylate,[1b,2] photochromism,[3] as in

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