

Picryl Derivatives of Benzo[1,2-*d*:4,5-*d'*]bistriazole and
Benzo[1,2-*d*:4,5-*d'*]bistriazole-4,8-dione (I)

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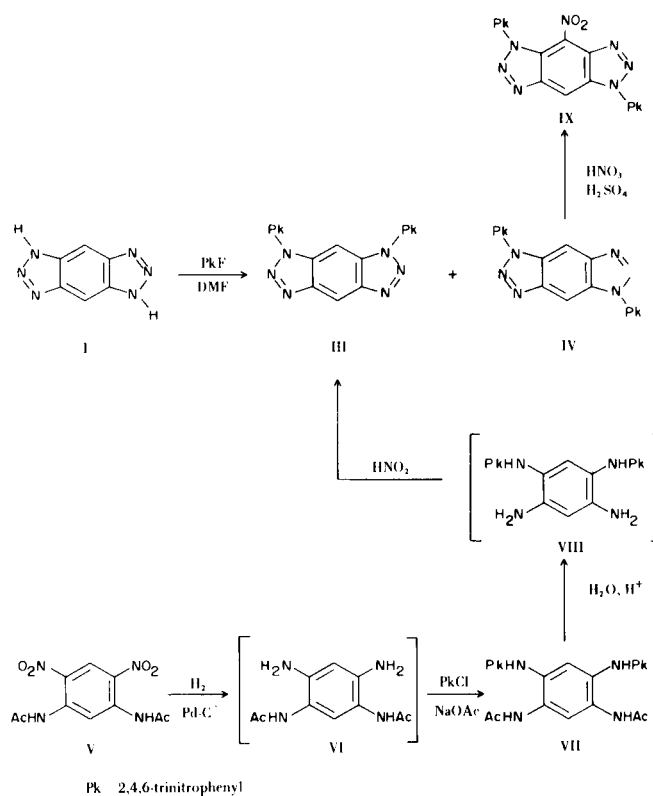
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In a previous communication from this laboratory it was reported that benzotriazole reacts with both picryl chloride and picryl fluoride to give 1-picrylbenzotriazole exclusive of any 2-picrylbenzotriazole (3). As an extension of this study we have examined the reactions of benzo[1,2-*d*:4,5-*d'*]bistriazole (I) and benzo[1,2-*d*:4,5-*d'*]bistriazole-4,8-dione (II) with picryl fluoride.

The reaction of I with two equivalents picryl fluoride gave a mixture of two dipicryl derivatives, which was resolved by extraction with hot acetone; one of the isomers is quite soluble and the other isomer is completely insoluble in this solvent. The acetone-soluble product was conclusively identified as 1,7-dipicrylbenzo[1,2-*d*:4,5-*d'*]bistriazole (III) by unambiguous synthesis starting with 1,5-bis(acetylamino)-2,4-dinitrobenzene (V). Hydrogenation of V in DMF provided a solution of 1,5-bis(acetylamino)-2,4-diaminobenzene (VI), which was treated with picryl chloride to yield 1,5-bis(acetylamino)-2,4-bis(picrylamino)benzene (VII). 1,5-bis(picrylamino)-2,4-diaminobenzene (VIII), produced *in situ* by hydrolysis of VII, was converted by nitrous acid to a product (III) that was identical in all respects with the acetone-soluble product. The assignment of the chemical shifts to the C-4 and C-8 protons of III in Table I is based upon the observation that the C-4 protons of 1-picrylbenzotriazoles are deshielded to a much greater extent than the corresponding C-7 protons (3).

The pmr spectrum of the acetone-insoluble product revealed that the protons of the two picryl groups are equivalent and that the C-4 and C-8 protons are also equivalent (see Table I). Thus, the compound is not 1,6-dipicrylbenzo[1,2-*d*:4,5-*d'*]bistriazole, which would have nonequivalent picryl groups and nonequivalent C-4 and C-8 protons. The product was nitrated to a mononitro derivative that has nonequivalent picryl protons. This result eliminates 2,6-dipicrylbenzo[1,2-*d*:4,5-*d'*]bistriazole, which, furthermore, would have the uncommon Dewar benzene nucleus. Therefore, the acetone-insoluble product must be 1,5-dipicrylbenzo[1,2-*d*:4,5-*d'*]bistriazole (IV) and its nitration product is 1,5-dipicryl-4-nitrobenzo[1,2-*d*:4,5-*d'*]bistriazole (IX).



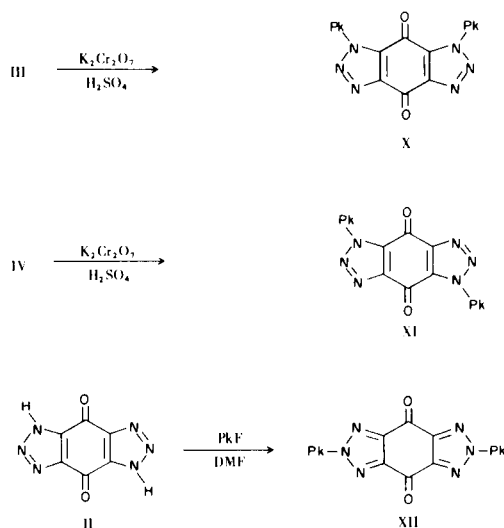
In contrast, II reacted with two equivalents of picryl fluoride to give a quantitative yield of a single dipicryl derivative for which four structures are conceivable. One of the structures, that of 1,6-dipicrylbenzo[1,2-*d*:4,5-*d'*]bistriazole-4,8-dione, was eliminated by the pmr spectrum of the product, which indicates that the compound has equivalent picryl groups. Two of the other possible isomers, 1,7-dipicrylbenzo[1,2-*d*:4,5-*d'*]bistriazole-4,8-dione (X) and 1,5-dipicrylbenzo[1,2-*d*:4,5-*d'*]bistriazole-

Table I

Benzo[1,2- <i>d</i> :4,5- <i>d'</i>]bistriazole	Picryl	Nmr Spectra (a)			Ir Spectra (b)		
		δ C-H (ppm)	C-4	C-8	J (cps)	C-H	ν (cm ⁻¹)
1,5-Dipicryl-	9.69 (s)	9.06 (s)	9.06 (s)		3080		1543, 1341
1,7-Dipicryl-	9.62 (s)	9.54 (d)	8.40 (d)	0.5	3082		1538, 1331
1,5-Dipicryl-4-nitro-	9.67 (s), 9.75 (s)		9.83 (s)		3089		1541, 1331
Benzo[1,2- <i>d</i> :4,5- <i>d'</i>]bistriazole-4,8-dione							
1,5-Dipicryl-	9.66 (s)				3093	1703	1549, 1335
1,7-Dipicryl-	9.63 (s)				3089	1719, 1704	1546, 1336
2,6-Dipicryl-	9.62 (s)				3090	1720	1548, 1347

(a) Determined with a Varian A-60A spectrometer as DMF solutions using TMS as an internal standard. Some of the compounds would not dissolve in DMF at ambient temperature; however, they dissolved in DMF at elevated temperatures and did not crystallize from the solutions when they cooled to ambient temperature. (b) Determined with a Perkin-Elmer spectrometer as potassium bromide disks.

4,8-dione (XI), were synthesized unequivocally by dichromate oxidation of III and IV, respectively. The ir spectrum of the product in question is significantly different from those of X and XI (see Table I); therefore, the compound is 2,6-dipicrylbenzo[1,2-*d*:4,5-*d'*]bistriazole-4,8-dione (XII). Apparently position 1 of II is much less nucleophilic than that of I. This observation is in agreement with those of others (4) who have concluded that the electron-withdrawing effect of quinone carbonyl groups is comparable to that of the nitro group.



EXPERIMENTAL.

CAUTION: MOST OF THE COMPOUNDS PREPARED IN THIS STUDY ARE EXPLOSIVES WITH IMPACT SENSITIVITIES COMPARABLE TO THAT OF 1,3,5-TRINITROHYDRO-*s*-TRIAZINE.

Elemental analyses were performed by M. J. Naranjo. Melting

points and explosion temperatures were obtained with a duPont 900 Differential Thermal Analyzer and are corrected.

Reaction of Benzo[1,2-*d*:4,5-*d'*]bistriazole (I) with Picryl Fluoride.

Benzo[1,2-*d*:4,5-*d'*]bistriazole (5) (0.40 g., 0.0025 mole) was dissolved in anhydrous *N,N*-dimethylformamide (15 ml.), and picryl fluoride (1.30 g., 0.0056 mole) was added. The mixture was stirred at 25° for 3 hours, then it was diluted with water (100 ml.). The solid was collected by filtration, washed with water and dried. The product was digested in boiling acetone (100 ml.) and filtered. The digestion was repeated and the combined filtrates were evaporated to dryness to yield a residue that was taken up in ethanol. The solid was removed by filtration, washed with ethanol, and dried at 100° to yield 0.65 g., (44%) of pure 1,7-dipicrylbenzo[1,2-*d*:4,5-*d'*]bistriazole (III), which did not melt, but exploded at 295°.

Anal. Calcd. for C₁₈H₆N₁₂O₁₂: C, 37.13; H, 1.04; N, 28.87. Found: C, 37.40; H, 1.04; N, 28.63.

The acetone-insoluble fraction was dried at 100° to give 0.81 g. (56%) of 1,5-dipicrylbenzo[1,2-*d*:4,5-*d'*]bistriazole (IV), explosion temperature 328°.

Anal. Calcd. for C₁₈H₆N₁₂O₁₂: C, 37.13; H, 1.04; N, 28.87. Found: C, 37.14; H, 1.12; N, 28.62.

1,5-Bis(acetylamino)-2,4-dinitrobenzene (V).

The acetylation of 1,5-diamino-2,4-dinitrobenzene to V with refluxing acetic anhydride has been reported (6); however, we were unable to obtain V by the procedure described. We found that the addition of a catalytic amount of sulfuric acid was necessary for complete acetylation. Thus, 1,5-diamino-2,4-dinitrobenzene (7) (5.0 g., 0.025 mole) was added to boiling acetic anhydride (50 ml.), and the resulting mixture was refluxed for one hour, treated with one drop of concentrated sulfuric acid, and refluxed an additional 10 minutes. The cooled solution was added to water (100 ml.) and the mixture was stirred until hydrolysis of the excess acetic anhydride was complete. The product was collected and recrystallized from acetic acid to yield 3.97 g. (56%), m.p. 228° [lit. (8) m.p. 228°].

1,5-Bis(acetylamino)-2,4-bis(picrylamino)benzene (VII).

Compound V (2.82 g., 0.01 mole) was hydrogenated in *N,N*-dimethylformamide (50 ml.) over 5% palladium on charcoal under 50 psi of hydrogen at 25° for one hour. The catalyst was removed

by filtration and the filtrate was treated with picryl chloride (6.0 g., 0.024 mole) and sodium acetate (2.0 g., 0.024 mole). The mixture was stirred at 25° for two days, then it was diluted with water (300 ml.) to precipitate the product, which was collected by filtration, washed with water, and recrystallized from acetone-ethanol to provide 2.46 g. (38%) of VII, m.p. 288° dec.

Anal. Calcd. for C₂₂H₁₆N₁₀O₁₄: C, 41.00; H, 2.50; N, 21.73. Found: C, 41.15; H, 2.23; N, 21.82.

1,7-Dipicrylbenzo[1,2-*d*:4,5-*d'*]bistriazole (III).

A solution of VII (0.64 g., 0.001 mole) in concentrated sulfuric acid (20 ml.) was treated dropwise with water (15 ml.) at such a rate that the temperature did not exceed 100°. The temperature of the mixture was held at 100° for 20 minutes, then it was lowered to 5° by cooling with an ice bath. Sodium nitrite (0.55 g., 0.008 mole), dissolved in a minimal amount of water, was added dropwise at 5-10°. The mixture was allowed to warm to room temperature and the solid that crystallized from solution was collected by filtration, washed with water and dried at 100° to yield 0.35 g. (60%) of III, identical in all respects with the acetone-soluble product of the reaction of I with picryl fluoride.

1,5-Dipicryl-4-nitrobenzo[1,2-*d*:4,5-*d'*]bistriazole (IX).

1,5-Dipicrylbenzo[1,2-*d*:4,5-*d'*]bistriazole (IV) (0.58 g., 0.001 mole) was added to a mixture of absolute nitric acid (10 ml.) and 20% oleum (10 ml.). The mixture was heated under reflux for one hour, cooled to 25°, and poured over crushed ice (~200 g.). The precipitated product was collected by filtration, washed with water, and recrystallized from acetone-ethanol to give 0.13 g. (21%) of IX, which does not melt, but explodes at 330°.

Anal. Calcd. for C₁₈H₅N₁₃O₁₄: C, 34.46; H, 0.80; N, 29.03. Found: C, 34.69; H, 0.67; N, 28.82.

1,7-Dipicrylbenzo[1,2-*d*:4,5-*d'*]bistriazole-4,8-dione (X).

A solution of III (0.40 g., 0.0007 mole) in concentrated sulfuric acid (10 ml.) was treated dropwise with a solution of potassium dichromate (0.7 g., 0.0024 mole) in hot concentrated sulfuric acid with the temperature controlled at 80-90°. After the addition was complete the mixture was poured over ice (~50 g.), and the solid was collected by filtration, washed with water and then with ethanol, and dried at 100° to give 0.24 g. (57%) of X, explosion temperature 257°.

Anal. Calcd. for C₁₈H₄N₁₂O₁₄: C, 35.31; H, 0.66; N, 27.45. Found: C, 35.79; H, 1.04; N, 27.83.

1,5-Dipicrylbenzo[1,2-*d*:4,5-*d'*]bistriazole-4,8-dione (XI).

A solution of potassium dichromate (1.2 g., 0.004 mole) in hot concentrated sulfuric acid (10 ml.) was added to a solution of IV (0.40 g., 0.0007 mole) at 80-90°. The resulting mixture was stirred at 80-90° for one hour, then it was poured over ice (~50 g.). The product was collected by filtration, washed successively with water, ethanol, and acetone, and dried at 100°. The yield of XI, explosion temperature 255°, was 0.22 g. (52%).

Anal. Calcd. for C₁₈H₄N₁₂O₁₄: C, 35.31; H, 0.66; N, 27.45. Found: C, 35.08; H, 0.84; N, 27.18.

2,6-Dipicrylbenzo[1,2-*d*:4,5-*d'*]bistriazole-4,8-dione (XII).

Picryl fluoride (1.50 g., 0.0065 mole) was added to a solution of benzo[1,2-*d*:4,5-*d'*]bistriazole-4,8-dione (II) (9) (0.60 g., 0.003 mole) in *N,N*-dimethylformamide (20 ml.), and the mixture was stirred at 25° for 16 hours. After the mixture was diluted with water (100 ml.), the solid was collected by filtration, washed successively with water and acetone, and dried at 100° to provide 1.76 g. (96%) of XII, explosion temperature 430°.

Anal. Calcd. for C₁₈H₄N₁₂O₁₄: C, 35.31; H, 0.66; N, 27.45. Found: C, 35.64; H, 0.70; N, 27.27.

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