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Synthesis and Properties of 1,2-Difluorodinitroethylene

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Synthesis and Properties of 1,2-Difluorodinitroethylene

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1,2-Difluorodinitroethylene was synthesized by flash vacuum pyrolysis of 1,2-difluorotetranitroethane. X-ray crystallography 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. 1,2-Difluorodinitroethylene reacted with alcohols to give alkyl fluoronitroacetates and with anthracene and cyclopentadiene to give Diels-Alder adducts.

There has been recent interest in the effect of electronegative substituents such as nitro1 and fluorine2 on the structural properties of olefins. Tetranitroethylene, the most electronegatively substituted olefin reported, is not sufficiently stable for convenient structural studies.3 This compound could be stored only under vacuum, apparently N(1)0-(1B) 1.208 (5) C(2)-F(2) 1.327 (5) sufficient for convenient structural studies.

Table I. Bond Lengths (Å) and Angles (deg) for trans-1,2-Difluorodinitroethylene

<table>
<thead>
<tr>
<th>Bond Length</th>
<th>Bond Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-F(1) 1.311 (5)</td>
<td>F(1)-C(1)-N(1) 112.3 (3)</td>
</tr>
<tr>
<td>C(1)-C(2) 1.284 (5)</td>
<td>C(1)-C(2) 1.476 (5)</td>
</tr>
<tr>
<td>N(1)-O(1A) 1.205 (5)</td>
<td>O(2A)-N(2)-O(2B) 127.0 (3)</td>
</tr>
</tbody>
</table>

The reaction of tetranitroethylene with alcohols to give alkyl dinitroacetates has been reported5. The products were explained on the basis of the initial formation of the unstable tetranitroethoxy ethers, which underwent loss of dinitro groups. 1,2-Difluorodinitroethylene reacted similarly with methanol, ethanol, and 2-propanol to give the corresponding fluoronitroacetates, reported previously from reactions of the alcohols with fluoronitromethy1 chloride5.
to be an extrt~incly reactive dienophile in Diels-Alder re- 

Fluoro-5,6-dinitrobicyclo[2.2.1]hept-2-ene in 49% yield. (d 

Temperature in methylene chloride gave 

I,12-dinitro-9,10-dihydro-9,10-ethanoanthracene, isolated 

Benzene monosolvate. The reaction of 1,2-di- 

The abovc procedure gave methyl fluoronitroacetate (0.202 

Methyl fluoronitroacetate. The reaction 

Isopropyl fluoronitroacetate. A 

This trap was found to contain 

volatile, 

This trap was found to contain 

volatile, 

Analyzed for C, H, N, F. Found: C, 46.4; H, 4.88; F, 11.51; N, 8.48. 

Etetyl Fluoronitroacetate. The reaction of 1,2-difluoro- 

methanol (100 mL) by the 

procedure gave methyl fluoronitroacetate (0.202 g, 29%). 

Methyl Fluoronitroacetate. The reaction 

11,12-Difluoro-11,12-dinitro-9,10-dihydro-9,10-ethano- 

A solution of 1,2-difluoro- 

11,12-dinitro-9,10-dihydro-9,10-ethanoanthracene benzene monosolvate, mp 192–193 °C: IR 1590.
A solution of 1,2-difluorodinitroethylen (0.299 g, 1.94 mmol) and freshly distilled cyclopentadiene (1.5 g, 23 mmol) in CHCl₃ (10 mL) was stirred under nitrogen for 10 min at ambient temperature. The solvent was evaporated and the residual oil was chromatographed (silica gel, CH₂Cl₂) to give 0.299 g (49% of endo-5,exo-6-difluoro-5,6-dinitrobicyclo[2.2.1]hept-2-ene: a linear decay of -121.5 to -0.28 e \text{Å}^{-1} over data collection, \theta/20 mode, scan width [29(\theta)] to [29(\theta)] = 0.56 \text{Å}^{-1}; range of hkl, 0 \leq h \leq 6, 0 \leq k \leq 13, and 0 \leq l \leq 14. Standard reflections 400, 040, 006 measured every 100 reflections showed a linear decay of ±15% over data collection, \theta/20 mode, scan width [29(\theta)] to [29(\theta)] = 0.56 \text{Å}^{-1}. 2\theta scan rate 60.0° min⁻¹ (rapid due to volatile crystal, full data set collected in 4 h); 855 reflections measured, 841 unique, 736 observed with Fₐ > 3σ(Fₐ). Data was corrected for Lorentz and polarization, and an empirical absorption correction was applied. The maximum and minimum transmission values were 0.77 and 0.72. Structure was solved by direct methods. The least-squares refinement minimized the quantity \sum \sqrt{[F_{o}-|F_{c}|]^2}, where w = 1/[σ²(|F_{o}|) + g(|F_{c}|)^2], g = 0.00023. Secondary extinction parameter p = 0.012 (1) in Fₐ. There were 92 parameters refined: atom coordinates, anisotropic thermal parameters for non-hydrogen atoms; the hydrogen atoms bonded carbon atoms (C-H distance set at 0.96 Å and angles involving H atoms idealized at tetrahedral or trigonal values, as appropriate. (Δ/σ)max = 0.04, R = 0.045, wR = 0.047, S = 1.41. Final difference Fourier excursions 0.16 and -0.18 e \text{Å}^{-3}. Atomic scattering factors from International Tables for Crystallography. The programs used for structure solution, refining, and plotting are part of SHELXTL.8

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(8) Tables of atom coordinates, bond distances and angles, structure factors, anisotropic thermal parameters, and hydrogen coordinates are included in the supplementary material.