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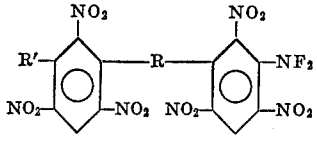
3,776,958 NITRODIFLUORAMINOPOLYAROMATIC COMPOUNDS

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Int. Cl. C07c 87/00
U.S. Cl. 260—576 5 Claims

ABSTRACT OF THE DISCLOSURE

Difluoraminonitropolyaromatic compounds corresponding to the formula



wherein R may be —CH=CH—, —CH_2—CH_2—, or 0 (zero), i.e., a direct ring carbon to ring carbon bond; and wherein R' may be H or —NF_2 and methods of preparing same. The compounds are of high energy density suitable as explosives, for use in detonators or as plasticizers or otherwise as components in explosive and propellant compositions.

BACKGROUND OF THE INVENTION

The invention set forth herein were made under, or in, the course of Purchase Order Nos. 58–0883 and 58–3246 under Contract No. AT(29–1)–789 with the United States Atomic Energy Commission.

A number of high energetic heat-stable explosives, such as TNT, picric acid, etc., derive their energy from 2,4,6-trinitrophenyl groups incorporated therein. However, many of such explosives are insensitive to initiation except by a very strong explosive shock as provided by detonators and/or other composite detonation assemblies. Trinitrophenyl type explosives are generally not susceptible to initiation by exploding bridgewire (EBW) techniques. Explosive compositions which would include the basic trinitrophenyl moiety which provides for highly energetic detonations and is characterized by other desirable properties such as heat stability, mechanical shock insensitivity, and the like, but which could be detonated by EBW techniques would be valuable additions to the available stock of explosive materials.

In classical electric high explosive detonator systems there is employed a fuse wire adjacent to which there is disposed a primary explosive such as mercury fulminate, lead azide, lead styphnate, or other deflagrating explosive material, in an amount sufficient to detonate a base charge of high explosive such as pentaerythritol tetranitrate (PETN), trimethylene trinitramine (RDX), tetryl or the like disposed adjacent thereto. The electrical current heats the fuse wire to the melting point igniting the sensitive primary material which then detonates the base charge producing a detonation or shock wave of sufficient magnitude to detonate a large quantity of more stable high explosive to subsequently produce most of the energy obtained in the detonation.

The primary materials employed in such classical detonators are very sensitive to mechanical shock and also to induced electrical or accumulated static charges so that extreme precautions are required to avoid inadvertent initiation. While satisfactory for usual blasting purposes, if appropriate precautions are observed, it will be noted that a relatively long and somewhat variable time period, i.e.,

a millisecond or greater, with a similar time period spread, elapses on application of the electrical current until the detonator ignites. It is not possible using such detonators to obtain a precise detonation time or precise sequencing or simultaneity of detonation in multiple detonation point arrays where time factors of the order of microseconds or less is of critical importance.

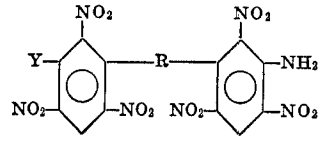
One approach developed in the prior art for obviating the difficulties associated with the use of the classical electric detonator involves the use of an exploding bridgewire to detonate a base or booster charge directly. For example, U.S. Pat. No. 3,040,660, issued June 26, 1962, to Lawrence H. Johnston, discloses such a device in which a bridgewire of a few thousandths of an inch diameter and a fraction of an inch in length is arranged in proximity to a quantity of an explosive of the detonating type (PETN) ordinarily used as a base or booster as described above. Another system employing an exploding bridgewire is disclosed in U.S. Pat. No. 3,158,098, issued Aug. 9, 1963, to Robert S. Reith et al. Such secondary base or booster explosive are substantially insensitive to spark or shock initiation but are sufficiently sensitive to be detonated by a shock produced by an exploding bridgewire with reasonable amounts of electrical energy delivered therethrough as a short time duration fast rising pulse therethrough. This arrangement greatly improves the precision and reproducibility of the time at which an initiating detonation can be made to occur. In usual practice such an arrangement may be employed for detonating the much more insensitive and highly energetic explosives such as TNT (trinitrotoluene) and other nitrated aromatic carbon compounds which can be detonated reliably only by means of a very strong shock.

A procedure for preparing certain monophenyl-fluoramine-nitro compounds by the liquid phase fluorination of nitro-substituted nitro-phenyl compounds is disclosed in Jour. Org. Chem. 38, 1387 (1968) by C. L. Coon, M. E. Hill and D. L. Ross. In such procedure an appropriate nitroaromatic amine dissolved in HF or acetonitrile as a solvent are fluorinated by bubbling fluorine through the solution. Such procedure is also disclosed in U.S. patent application Ser. No. 748,569, filed July 29, 1968 by Marion E. Hill et al.

SUMMARY OF THE INVENTION

The present invention relates generally to processes for producing nitrated polyaromatic hydrocarbons having difluoramino substituents therein and, more particularly, to processes for producing compounds containing a pair of trinitrophenyl groups joined by certain linkages, at least one of which phenyl groups is provided with a difluoramine substituent, and to novel products produced thereby which are appropriately sensitized and have other properties especially useful in an exploding bridgewire (EBW) detonation system.

The starting materials used in producing the novel compounds of the invention correspond to the following structural formula:

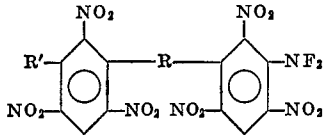


wherein Y may be —H or —NH_2 and R may be —CH=CH—, —CH_2—CH_2—, or a direct ring carbon to ring carbon bond.

The indicated starting material is dissolved or dispersed in a suitable solvent such as hot acetonitrile and is then cooled to below about 0° C. to below about −10° C. while disposed in a suitable reactor, e.g., a polytetra-

fluoroethylene type plastic reactor. The system is flushed with an inert gas such as nitrogen and then a mixture of fluorine gas with nitrogen is bubbled through the solution while stirred for several hours, usually at least about 2–3 hours until the reaction is complete. Gaseous mixtures of the order of 75% N_2-25% F_2 to 50% N_2-50% F_2 can be used. Residual fluorine is swept from the system with nitrogen and the solution is warmed to about 25° C. Methylene chloride in excess volume is added and silica gel together with anhydrous magnesium sulfate or the latter material alone is also added to remove residual HF formed in the reaction on stirring the mixture for about 1 hour. The silica gel and $MgSO_4$ are filtered from the solution and the solution is concentrated by evaporating the solvents at ambient temperature. A solvent such as successive portions of chloroform are added to the solution to precipitate a crude product. The product can be purified by dissolving in warm ethyl acetate, filtering out residual solid, evaporating some of the ethyl acetate and adding hot chloroform and cooling to recrystallize the product. The filtered product is washed with cold chloroform and is dried, in vacuo, to provide a purified product. Crude products in methylene chloride solvent and/or residual mother liquor fractions may also be purified by passage through silica gel chromatography columns.

The product compounds correspond to the formula



wherein R may be —CH=CH—, —CH_2—CH_2—, or 0, i.e., a direct bond. Where R is 0 and R′ is NF_2 the compound is 3,3′-bis(difluoroamino)-2,2′,4,4′,6,6′-hexanitrobiphenyl (FDIPAM) where R is —CH=CH— and R′ is H, the compound 3-difluoramino-2,2′,4,4′,6,6′-hexanitrostilbene (DHNS); and where R is 0 and R′ is H, the compounds is 3-difluoramino-2,2′,4,4′,6,6′-hexanitrobiphenyl (DHNB).

The crystalline products have highly energetic explosive qualities and are adapted to initiation by exploding bridgewire (EBW) techniques. The compounds are also subject to initiation by impact, shock, friction, rapid heating to somewhat lesser degree than explosive initiator compound; however, in view of the explosive nature thereof appropriate handling procedures should be used. Likewise precautions from toxicity, skin staining or skin contact burning are advisable.

Accordingly it is an object of the invention to provide novel nitrofluoramino-polyl-aromatic compounds for use as detonators, explosives, propellants and the like.

Another object of the invention is to provide certain nitro-difluoramino-biphenyl and -stilbene aromatic hydrocarbon suitable for use in exploding bridgewire explosive initiators.

Other objects and advantageous features of the invention will be apparent in the following description:

DESCRIPTION OF PRFERRED EMBODIMENTS OF THE INVENTION

For use in an exploding bridgewire detonator system the compositions of the invention can be employed in the same manner as those of the prior art. Generally the compositions are disposed in proximity or in contact with a very fine wire, i.e., bridgewire connected across a pair of current carrying conductors. The wire may be, for example, a 38 micron gold wire, fine nickel-chromium alloy, tungsten wire, gold wire and stainless steel, in sizes, e.g., of 0.001 to 0.010 inch over even larger sizes. A plus of electrical energy of amperage and voltage with circuit characterastics well known in the art may be switched by means well known in the art from a capacitor or other electrical energy pulse supply source across the bridge through said conductors to explode the bridgewire. The detonation shock from the bridgewire is communicated to the composition of the invention in which a highly energetic detonation ensues. In usual practice a stable high explosive such as a nitrated aromatic compound, e.g., TNT (trinitrotoluene) is disposed in proximity to or in contact with the detonating composition and is in turn detonated by the detonation shockwave produced by the detonator compositions.

A modification of the foregoing system employable with the present compositions are shown, for example, in a report No. LADC–6288 by James H. Blackburn et al., on the general subject of "Exploding Bridgwire Detonators," available from the Office of Technical Services, Department of Commerce, Washington, D.C. Other exploding bridgewire detonator systems, likewise employable, are disclosed in U.S. Pat. No. 3,040,660, issued June 26, 1962, to L. H. Johnston, for Electrical Initiator With Exploding Bridgewire; U.S. Pat. No. 3,158,098, issued Nov. 24, 1964 to R. J. Reithel for "Low Voltage Detonator System"; and U.S. Pat. No. 2,988,994, issued June 20, 1961 to Carl W. Fleischer, Jr., et al., for "Shaped Charge With Cylindrical Liner."

Further details relating to the compositions of the invention will be set forth in the following illustrative examples.

With respect to the experimental procedures it may be noted that fluorine as obtained from the manufacturer was always diluted in a stream with nitrogen prior to fluorination. Unless otherwise noted, chemicals were used as received from the manufacturer.

Melting points reported are uncorrected and were obtained in a capillary using a Mel-Temp melting point apparatus. NMR data were obtained using a Varian HA–100 NMR spectrometer. Values for ^1H chemical shifts are given in δ units with respect to tetramethysilane as internal reference, and values for the ^{19}F chemical shifts are given in φ units with respect to trichlorofluoromethane as an internal reference. In NMR descriptions, s.= singlet, d.=doublet, t.=triplet, q.=quadruplet, m.= multiplet. Infrared spectra were run on a Perkin-Elmer Model 137 Infracord spectrophotomer. In IR descriptions, s.=strong, m.=medium, w.=weak, b.=broad.

Thin-layer chromatography was carried out on Eastman Chromagram sheets of silica gel with fluorescent indicator. Anhydrous magnesium sulfate was added to reaction mixtures from fluorinations in acetonitrile to remove residual hydrogen fluoride. Since magnesium sulfate was slightly soluble in acetonitrile, addition of methylene chloride to the acetonitrile solution reduced this solubility. To remove the small amount of magnesium sulfate that dissolved from the isolated crude product of the fluorination, the product was dissolved in methylene chloride or ethyl acetate and filtered. Elution of difluoraminonitroaromatic compounds in column chromatography was detected by spraying a spot of the eluate on filter paper with a 0.2% solution of N,N,N′,N′-tetramethyl-p-phenylenediamine dihydrochloride in 50% methylene chloride and ethanol (TMPDA reagent); thin layer chromatograms were also sprayed with TMPDA reagent, which turned blue in the presence of strong oxidizers such as NF_2-nitroaromatic compounds. Often the blue color changed to yellow at or above ambient temperature. Densities were determined using a Fisher-Davidson gravitometer.

EXAMPLE I

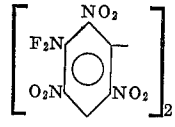
(1) Bis(difluoramino)hexanitrobiphenyl (FDIPAM)

A 2.0 g. sample of DIPAM (3,3′-diamino-2,4,6,2′,4′,6′-hexanitrobiphenyl) was dissolved in 250 ml. hot acetonitrile (Nanograde). The yellow solution was cooled to 0–10° and was poured into a Kel-F reactor. The system was flushed with nitrogen, and 25% fluorine in nitrogen was bubbled through the stirred solution at 60 ml./min. for 3 hr. The yellow mixture became red-brown after a

short period of time, and after 30 min. the color began to lighten gradually. When the fluorination was complete the system was flushed with nitrogen, and 250 ml. methylene chloride was added. Anhydrous magnesium sulfate and silica gel were then added to absorb traces of hydrogen fluoride. Since magnesium sulfate is partially soluble in acetonitrile it was necessary to add methylene chloride to the mixture. The mixture was swirled for 20 min. and filtered. Evaporation of the filtrate was carried out at ambient temperature because excessive heating of the crude product caused darkening of the material. The evaporation was stoppd shortly before the solution became an oil, and 75 ml. warm chloroform was added. Crystallization gave 0.4 g. product, M.P. 219–225° (dec.). The mother liquor gave an additional 0.1 g. by using the same procedure. The combined solids (0.5 g.) were dissolved in warm ethyl acetate, and a small amount of insoluble material was removed. The resulting clear solution was reduced in volume but was not allowed to form an oil. Addition of 30 ml. hot chloroform and subsequent crystallization gave 0.26 g. product, M.P. 228–230° (dec.). Using this procedure a total of 11% of the theoretical yield was obtained. The mother liquor was combined with those of other runs and was purified by column chromatography using a 0.8" x 20" column of silica gel prepared in chloroform. The oil was dissolved in a minimum amount of acetonitrile and was placed on the column. Elution was carried out with chloroform, and the desired fractions, when collected, gave a positive test with TMPDA reagent.

Properties of 3,3'-bis(difluoramino-2,2',4,4',6,6'-hexanitrobiphenyl (FDIPAM)

Structure:



Empirical formula: $C_{12}H_2F_4N_8O_{12}$.
Molecular weight: 526.19.
Appearance: Pale yellow crystals.
Melting point: 234–237° C. dec.
Crystal density: 1.82.
Olin drop weight test: 3–4 cm./2 kg. at 19° C., HMX 36 cm.
Differential thermal analysis: 10° C./min. from 25° C., 204° C. exploded.
Vacuum thermal stability: 1.88 cc./g./48 hr. and 2.83 cc./g./96 hr. at 100° C.

Analyses.—Calculated (percent): C, 27.39; H, 0.38; N, 21.30. Found (percent): C, 27.99; H, 0.62; N, 21.22.

$\lambda_{cm.-1}^{nujol}$: 722 (s.), 737 (m.), 879 (s.), 928 (m.), 976 (m.), 1333 (s.), 1560 (s.).

Sensitivity to handling: FDIPAM is stable upon storage at ambient temperature for long periods of time and, with the usual precautions, can be easily handled.
Explosive bridgewire test: More sensitive to initiation than PETN.

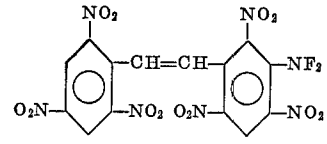
EXAMPLE II

(2) 3-difluoramino-2,4,6,2',4',6'-hexanitrostilbene

A mixture of 6.0 g. of finely divided 3-amino-2,4,6,2',4',6'-hexanitrostilbene and 300 ml. acetonitrile was boiled for 15 min. to disperse and partially dissolve the compound. The slurry was then poured into a Kel-F reactor. The system was flushed with nitrogen and cooled to −10°. A 60 ml./min. stream of 30% fluorine, 70% nitrogen was bubbled through the stirred reaction mixture from 2 mm. I.D. Teflon tubing. During the first three hours, the suspension darkened from green-yellow to red-brown. At the fourth hour the reaction mixture was orange and nearly clear. The fluorine was turned off when the liquid was clear and yellow; the total fluorination time was five hours. Residual fluorine was swept from the system with nitrogen while the reaction mixture was warmed with a 25° bath. The liquid, which darkened slightly on warming to 25°, was poured into 300 ml. of methylene chloride. Approximately 50 g. of silica gel and 100 g. of anhydrous magnesium sulfate were added to remove residual HF and the mixture was stirred at least 1 hr. A tan solid was obtained after filtration and evaporation in vacuo. Crystallization was accomplished by dissolving the material in 50 ml. of warm ethyl acetate, filtering to remove a trace of solid, and adding 100 ml. hot chloroform to the filtrate. After cooling the mixture to 0°, the light tan solid was collected, washed with chloroform, and dried in vacuo. The 3-difluoramino-2,4,6,2',4',6'-hexanitrostilbene, M.P. 205–208° (dec.), weighed 2.7 g., 42% of theory. An additional 0.5 g. of product was obtained from the mother liquor.

Properties of 3-difluoramino-2,2',4,4',6,6'-hexanitrostilbene (DHNS)

Structure:



Empirical formula: $C_{14}H_5F_2N_7O_{12}$.
Molecular weight: 501.24.
Appearance: Pale yellow crystals.
Melting point: 205–208° C. dec.
Crystal density: 1.76.
Olin drop weight test: 23–25 cm./2 kg. at 20° C., HMX 36–38 cm.
Differential thermal analysis: 200° C. exo (160–225° C. full range of exo).

Analyses.—Calculated (percent): C, 33.55; H, 1.01; F, 7.58; N, 19.56. Found (percent): C, 33.86; H, 1.15; F, 7.50; N, 19.09.

NMR in CH_3CN.—Peak: −71.9φ, singlet. Assignment: $-NF_2$.
Sensitivity to handling. Stable to storage in air for 3 weeks; easily develops a static charge when handled with a spatula; strongly "adsorbs" HF, CH_3CN, $CH_3COOC_2H_5$
Exploding bridgewire test: Less sensitive to initiation than PETN.

Synthesis of difluoraminohexanitrobiphenyl (DHNB)

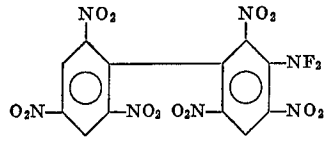
A stirred solution of 16.0 g. of 3-amino-2,2',4,4',6,6'-hexanitrobiphenyl in 500 ml. of dry acetonitrile in a 1 l. three-neck glass flask was cooled to −5 to 0° C. while air was flushed from the system by a stream of nitrogen. Fluorination was conducted over a 5 hr. period by bubbling a mixture of 25% fluorine in nitrogen through the cold liquid at 120 ml./min. The clear, pale green reaction mixture darkened within a few minutes, began to lighten after 3 hrs. and was red-orange when the fluorine was shut off. Toxic gases were flushed with the system by a stream of nitrogen. Then 500 ml. of methylene chloride and 40 g. of anhydrous magnesium sulfate were stirred with the reaction mixture for 1 hr. at ambient temperature. The liquid was filtered and evaporated to give 18 g. of crude DHNB, a brown solid. This solid was dissolved in 40 ml. of methylene chloride, the solution was placed on a column (4 x 40 cm.) of silica gel (ca. 150 g.), and eluted with a mixture of 50% hexane in methylene chloride. Solid which precipitated near the top of the column slowly redissolved during the elution, and a satisfactory development was obtained. The eluant was examined by the N,N,N',N'-tetramethyl - p - phenylenediamine dihydrochloride (TMPDA) reagent spot test and by thin layer chromatography (TLC). TLC analysis showed that four compounds were eluted, all giving positive TMPDA tests

for NF (or other strong oxidizers). Eluant containing the second compound eluted was evaporated to give 9.0 g. of crude DHNB in 56% yield. A hot solution of the crude DHNB in 800 ml. of chloroform was filtered and then concentrated on a hot plate to about 300 ml. until crystallization began. The liquid was stored at ambient temperature until the crystallization was complete and then cooled in an ice bath. Yellow, crystalline DHNB (M.P. 205–208° C. dec.) was filtered, washed with cold chloroform and dried in vacuo to give 5.1 g., 29% yield.

Analysis.—Calcd. for $C_{12}H_3F_2N_7O_{12}$ (percent): C, 30.33; H, 0.63; F, 8.00; N, 20.63. Found (percent): C, 30.52; H, 0.74; F, 7.7; N, 20.66.

Properties of 3-difluoramino-2,2',4,4',6,6'-hexanitrobiphenyl (DHNB)

Structure:



Empirical formula: $C_{12}H_3F_2N_7O_{12}$.
Molecular weight: 475.21.
Appearance: Small yellow crystals.
Melting point: 234–237° C. dec.
Crystal density: 1.83.
Spark sensitivity: >75 mj., PbN_3 5–10 mj.
Man's capacity: 15 mj.
Olin drop weight test: 4–5 cm./2 kg. at 22° C., HMX 35–36 cm./2 kg.
Differential thermal analysis: Exo 178° C. (onset), 225° C. (peak).
Analysis.—Calculated (percent): C, 30.33; H, 0.63; F, 8.00; N, 20.63. Found (percent): C, 30.52; H, 0.74; F, 7.7; N, 20.66.
NMR in acetone-d_6.—Peak: -60.9φ, singlet; 0.57τ, singlet; 0.50τ, triplet; $J_{H,\ NF} \sim 1$ c.p.s. Assignment: NF_2; 3',5'-protons; 5-proton. Exploding bridgewire test: Nearly as sensitive to initiation as PETN.

3-amino-2,2',4,4',6,6'-hexanitrobiphenyl (amino-HNB)

Amino-HNB used in the foregoing example was prepared as follows:

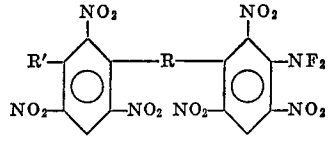
Anhydrous ammonia was bubbled from a coarse fritted glass tube through a magnetically stirred, boiling solution of 88 g. of pure 3-methoxy-2,2',4,4',6,6'-hexanitrobiphenyl (M.P. 195–196° C.) in 880 ml. of dry acetonitrile in a 2-liter Erlenmeyer flask for 15 min. Excess ammonia was removed by boiling the clear red liquid an additional 15 min. Such methoxyhexanitrobiphenyl was recrystallized from a mixture of acetone and hexane. Then 1 liter of hot ethanol was added with stirring to the hot reaction mixture. The flask was removed from the hot plate and stirring was continued. Crystallization began after a few minutes. After the liquid had cooled to ambient temperature, the flask was placed in an ice water bath. Pure amino-HNB was filtered, washed with cold ethanol, and dried in vacuo to give 62.4 g. of bright yellow crystals, M.P. 221–222° C. A second batch weighing 18.7 g., M.P. 219–221° C., was obtained by dissolving the residue from the mother liquor in 300 ml. of boiling acetonitrile and adding 250 ml. of hot ethanol to this hot solution. The total yield, 81 g., corresponded to 95% theoretical. TLC analysis (benzene, silica gel) of both samples showed no impurities.

The exploding bridgewire tests were run with a Reynold's Industries header, type 167–2810, which has a gold wire 30 mils long and 1.5 mils in diameter. The sample was pressed in a brass bushing which was already glued to the header. Dimensions of the pressed sample were 300 mils long and 150 mils in diameter. Samples were weighed to the nearest 0.1 mg. and pressed to a density in the range 45 to 55% of the crystal density of the compound. All samples were ground in 50 mg. portions with a mortar and pestle; gloves and a protective shield were used for this operation. The sample particle size (0.01 to 0.03 mm.) was determined microscopically with a micrometer having a 2 mm. line graduated to 0.01 mm. divisions. Criteria used to identify a detonation were the sound of explosion and the appearance of the brass fragments from the bushing. PETN (military specifications) was used as a standard. The burst amperage was determined at the time of maximum voltage across the wire.

While there has been described in the foregoing what may be considered to be preferred embodiments of the invention, modifications within the skill of the art may be made therein without departing from the teachings of the invention and it is intended to cover all such as fall within the scope of the appended claims.

What we claim is:

1. A difluoraminonitropolyaromatic compound corresponding to the formula



wherein R may be —CH=CH—, —CH—CH_2— or a direct ring carbon to ring carbon bond and R' may be H or —NF_2.

2. A compound as defined in claim 1 selected from the group consisting of 3,3'-bis(difluoroamino)-2,2',4,4',6,6'-hexanitrobiphenyl, 3-difluoroamino - 2,2',4,4',6,6' - hexanitrostilbene and 3-difluoramino - 2,2',4,4',6,6'-hexanitrobiphenyl.

3. A compound as defined in claim 2 comprising 3,3'-bis(difluoramino)2,2',4,4',6,6'-hexanitrobiphenyl.

4. A compound as defined in claim 2 comprising 3-difluoramino2,2',4,4',6,6'-hexanitrostilbene.

5. A compound as defined in claim 2 comprising 3-difluoramino-2,2',4,4',6,6'-hexanitrostilbene.

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ROBERT V. HINES, Primary Examiner

U.S. Cl. X.R.

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