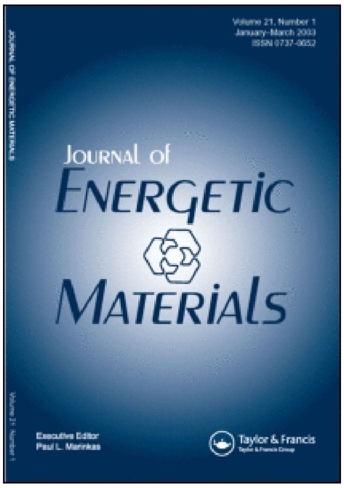

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Synthesis of polynitro and azido diesters of pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-2,4-dicarboxylic acid

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To cite this Article Guan, Xiao-Pei , Su, Zhuang , Du, Jian-Wei , Sun, Jian-Guang and Yu, Yong-Zhong(1997) 'Synthesis of polynitro and azido diesters of pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-2,4-dicarboxylic acid', Journal of Energetic Materials, 15: 2, 139 — 149

To link to this Article: DOI: 10.1080/07370659708216078

URL: http://dx.doi.org/10.1080/07370659708216078

SYNTHESIS OF POLYNITRO AND AZIDO DIESTERS OF PENTACYCLO[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]NONANE-2,4-DICARBOXYLIC ACID

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ABSTRACT

Homocubane-2,4-dicarboxylic acid (**6**) was synthesized starting from cyclopentadiene and 2,5-dibromobenzoquinone (**3**). Six polynitro and azido diesters of **6** were also synthesized as advanced energetic plasticizers. The results of DTA indicated that these compounds (**8a~8f**) are quite thermally stable.

INTRODUCTION

The development of high performance solid rocket propellants has stimulated interest in energetic cage molecules[1]. The large strain energy of the cage skeleton coupled with energetic substituents releases more energy than the usual energetic materials. Cage molecules, which can serve as energetic

Journal of Energetic Materials Vol. 15, 139-149 (1997)
Published in 1996 by Dowden, Brodman & Devine, Inc.

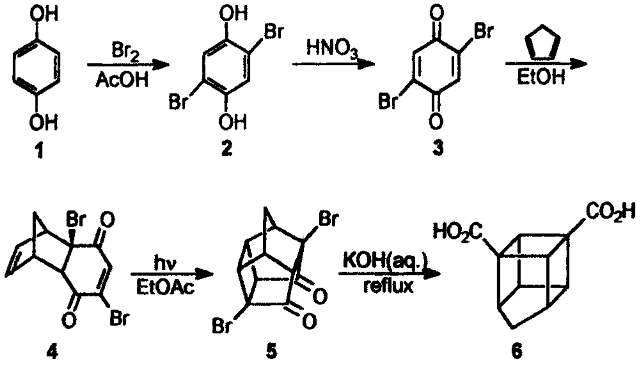
plasticizers, rocket fuels and oxidizers, are also expected to provide substantially improved propellant ingredients[2]. To be a useful and better plasticizer, a compound, which should be a stable organic ester or ether possessing energetic functional groups such as nitro, fluoronitro, azido, etc., must have low volatility and a low melting point.

The high symmetry of cubane-1,4-diesters usually results in high crystallinity and a high melting point[2a]. Therefore, our objective was to determine if less symmetrical cage molecules could be used as precursors in the construction of energetic plasticizers. Toward this end, we synthesized homocubane-2,4-dicarboxylic acid (**6**), which is less symmetrical than cubane-1,4 or 1,3-dicarboxylic acids and is more conveniently obtained[3]. This paper also presents some of our research into the synthesis of polynitro and azido esters of homocubane-2,4-dicarboxylic acid (**8a~8f**) and preliminary evaluation of their suitability as advanced energetic plasticizers.

RESULTS

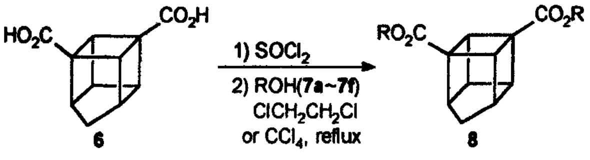
The synthesis of homocubane-2,4-dicarboxylic acid (**6**) from readily available and inexpensive starting materials is shown in Scheme 1. Treatment of hydroquinone (**1**) with 2 mol Br_2 in AcOH afforded 2,5-dibromohydroquinone (**2**), which was further oxidized with HNO_3 to give 2,5-dibromobenzoquinone (**3**). Cycloaddition of cyclopentadiene to **3** afforded the expected Diels-Alder adduct

(4) which was subsequently converted into the corresponding dibromotrishomocubanedione **5**. Homocubane-2,4-dicarboxylic acid (**6**) was then obtained in high yield via Favorskii rearrangement of **5**.



Scheme 1

Reflux with $SOCl_2$ converted **5** into the corresponding bis(acid chloride). Subsequent condensation with the alcohols (**7a**~**7f**) in $ClCH_2CH_2Cl$ or CCl_4 under reflux afforded the respective target compounds in high yields. In the presence of pyridine, the esterification of the corresponding azido alcohols proceeded smoothly at room temperature.



a, R= $-CH_2C(NO_2)_3$;
b, R= $-CH_2C(NO_2)_2F$;
c, R= $-CH_2C(NO_2)_2CH_2N(NO_2)CH_3$;
d, R= $-CH_2CH_2N_3$;
e, R= $-CH(CH_2N_3)_2$;
f, R= $-CH_2CH(N_3)CH_2N_3$.

Scheme 2

All the esters are liquids except **8a** and **8b**, which have melting points at 85°C and 62°C respectively. For comparison, cubane-1,4-bis(trinitroethylester) has a relatively high melting point of 159°C[4].

The results of DTA (see Table 1) indicated that these compounds are quite thermally stable. Further studies are being undertaken to evaluate them as possible advanced energetic plasticizers.

TABLE 1

DTA results for **8a**~**8f** (heating rate: 10°C/min)

Compounds:	**8a**	**8b**	**8c**	**8d**	**8e**	**8f**
T_m(°C)	220	259	228	235	216	223

EXPERIMENT SECTION

Melting points are uncorrected. IR spectra were recorded on a Shimadzu IR-408 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian EM-360L spectrometer and a Brucker ARX-400 spectrometer respectively. MS were measured with a Finnigan-Mat TSQ-45B instrument. Elemental analyses were performed on a Carlo Erba model 1106. DTA measurements were carried out on a BOIF PCR-1 differential thermal analyzer.

2,5-Dibromohydroquinone (2)

A suspension of hydroquinone **1** (110 g, 1.00 mol) in glacial acetic acid (300 mL) was stirred rapidly while bromine (320 g, 2.00 mol) was added dropwise so that the mixture remained gentle reflux. After cooling to room temperature and filtration, the crud product was recrystallized from acetic acid to give **2** as a colorless microcrystalline solid (216 g, 80.6%), m.p. 186.2~187.0°C (lit[5] 185~186°C). IR(KBr): 3250(s), 1425(s), 1197(m), 792(m)cm^{-1}. Anal. Calcd. for $C_6H_4O_2Br_2$: C, 26.90; H, 1.50; Found: C, 26.95; H, 1,37.

2,5-Dibromobenzoquinone (3)

To a suspension of 2,5-dibromohydroquinone (215 g, 0.802 mol) in water (200 mL) was added dropwise with vigorous stirring HNO_3 (68%, 120 mL). Then the reaction mixture was stirred at 60°C for further 0.5 h. After cooling to r.t., the crud product was collected by suction filtration and washed with cold water until neutral. Recrystallization from EtOAc afforded pure **3** as yellow prism crystals (180 g, 84.5%), m.p. 188.0~189.0°C (lit[6] 189~190°C). IR(KBr): 1656(s), 1587(m), 1190(m), 990(s)cm^{-1}. ^{1}H NMR($CDCl_3$): δ 7.52(s, 2H) ppm. MS(EI): *m/z* 268(27), 266(53), 264(28) (M^+). Anal. Calcd. for $C_6H_2O_2Br_2$: C, 27.10; H, 0.76; Found: C, 27.13; H, 0.72.

endo-2,5-Dibromotricyclo[6.2.1.0^{2,7}]undeca-4,9-diene-3,6-dione (4)

To a suspension of 3 (53.2 g, 0.200 mol) in ethanol (300 mL) was added freshly cracked cyclopentadiene (13.9 g, 0.211 mol), and the mixture was stirred at room temperature for 4h. After filtration, the crud products was recrystallized from ethanol to yield 4 as light yellow crystals (62.5 g, 94.1%), m.p. 134.0~135.0°C (lit[7] 130~131°C). IR(KBr): 1684(s), 1671(s), 1583(m), 1240(m), 770(m)cm^{-1}. ^{1}H NMR($CDCl_3$): δ 1.90, 2.04(ABq, J_{AB}=9.6Hz, 2H), 3.5~3.9(m, 3H), 6.09(m, 2H), 7.24(s, 1H)ppm. MS(EI): *m/z* 330(12), 332(22), 334(15) (M^+). Anal. Calcd. for $C_{11}H_8Br_2O_2$: C, 39.80; H, 2.43; Found: C, 39.66; H, 2.38.

1,9-Dibromopentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (5)

A benzene solution of 4 (50.0 g, 0.151 mol) was carefully purged with dry N_2 for 10 min. The solution was then irradiated with a 500w high pressure mercury vapor lamp (Pyrex filter) at room temperature. The reaction was monitored by TLC. Removal of the solvent in vacuo and recrystallization of the crud product from acetic acid afforded pure 5 as colorless crystals (45.2 g, 90.4%), m.p. 188.3~189.0°C (lit[7] 185~186°C). IR(KBr): 1769(s), 1755(s), 1078(m)cm^{-1}. ^{1}H NMR($CDCl_3$): δ 1.63, 2.12(ABq, J_{AB}=11.6Hz, 2H), 2.5~3.4(m, 6H)ppm. MS(EI): *m/z* 330(51), 332(62), 332(50) (M^+). Anal. Calcd. for $C_{11}H_8Br_2O_2$: C, 39.80; H, 2.43; Found: C, 39.78; H, 2.50.

Pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-2,4-dicarbxylic acid (6)

A mixture of **5** (26.0 g, 78.3 mmol) and 30% KOH aqueous solution (260 mL) was refluxed for 2h. The solution was cooled to below 15°C and acidified to pH 2 by dropwise addition of hydrochloric acid with stirring in an ice-water bath. The solid was filtered off and recrystallized from water (charcoal) to yield **6** as colorless crystals (13.2 g, 81.8%), m.p. 203.3~204.5°C. IR(KBr): 3300~2400(s), 1715(s), 1418(m), 1312(m), 1278(w), 1243(m)cm^{-1}. ^{1}H NMR(acetone-d_6): δ 1.82(s, 2H), 3.2~3.8(m, 6H), 4.51(s, 2H)ppm. ^{13}C NMR(acetone-d_6): δ 39.0(d), 43.6(d), 45.0(t), 45.9(d), 47.0(d), 48.2(s), 48.4(d), 50.9(d), 53.6(s), 172.4(s), 173.4(s)ppm. MS(CI/CH$_4$): *m/z* 207(M$^+$+1, 0.4), 206(M$^+$, 0.5), 189(M$^+$–OH, 100), 116(M$^+$–2CO$_2$H, 35). Anal. Calcd. for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89; Found: C, 64.26; H, 4.90.

Pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-2,4-bis(trinitroethylester) (**8a**)

The mixture of homocubane-2,4-dicarboxylic acid (**6**) (2.3 g, 11 mmol) and SOCl$_2$ (25 mL) was refluxed for 4h. Excess SOCl$_2$ was removed in vacuo to yield the crude acid chloride as a slightly yellow brown solid, which was refluxed with trinitroethanol (3.8 g, 21 mmol) in ClCH$_2$CH$_2$Cl (25 mL) for 24h. After cooling to r.t., the mixture was washed with NaHCO$_3$ (aq.), dried over MgSO$_4$. Removal of solvent in vacuo and crystallization of the crude product in CCl$_4$ afforded **8a** as colorless needle crystals (4.4 g, 74%), m.p. 84.9~85.5°C. IR(KBr): 1748(s), 1606(s), 1595(s), 1303(s), 1200(m), 1165(m)cm^{-1}. ^{1}H NMR(CDCl$_3$): δ 1.88(s, 2H), 3.2~3.8(m, 6H), 5.39(s, 4H)ppm. MS(CI/CH_4): *m/z* 561(M^++C_2H_5, 25), 532(M^+, 22), 352(M^+-$OCH_2C(NO_2)_3$, 100). Anal. Calcd. for $C_{15}H_{12}N_6O_{16}$: C, 33.85; H, 2.27; N, 15.79; Found: C, 33.73; H, 2.12; N, 15.80.

Pentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane-2,4-bis(dinitrofluoroethylester) (8b)

8b was prepared in 71% yield as colorless crystals according to the procedure described for the preparation of **8a**, m.p. 61.2~62.8°C. IR(KBr): 1739(s), 1608(s), 1310(s), 1200(m), 1163(m)cm^{-1}. ^1H NMR($CDCl_3$): δ 1.88(s, 2H), 3.2~3.8(m, 6H), 5.21(d, J_{HF}=16.2Hz, 4H)ppm. MS(CI/CH_4): *m/z* 479(M^++1, 3), 325(M^+-$OCH_2C(NO_2)_2F$, 100). Anal. Calcd. for $C_{15}H_{12}N_4O_{12}F_2$: C, 37.67; H, 2.53; N, 11.71; Found: C, 37.68; H, 2.35; N, 11.71.

Pentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane-2,4-bis(2,2,4-trinitro-4-azapentylester) (8c)

Essentially the same procedure described for the preparation of **8a** was used. Chromatography of the crude product on silica gel eluting with C_6H_6/CH_2Cl_2 (1:1) gave pure **8c** (87%) as a colorless clear oil. IR(neat): 1743(s), 1570(s), 1541(s), 1317(m), 1279(s), 1161(m)cm^{-1}. ^1H NMR($CDCl_3$): δ 1.85(s, 2H), 3.1~3.8(m, 6H), 3.41(s, 6H), 4.97(s, 8H)ppm. MS(CI/CH_4): *m/z* 619(M^++1, 2), 395(M^+-$OCH_2C(NO_2)_2CH_2N(NO_2)CH_3$, 100). Anal. Calcd. for $C_{19}H_{22}N_8O_{16}$: C, 36.90; H, 3,59; N, 18.12; Found: C, 36.98; H, 3.66; N, 18.01.

Pentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane-2,4-bis(2-azidoethylester) (**8d**)

The mixture of homocubane-2,4-dicarboxylic acid (**6**) (2.4 g, 12 mmol) and $SOCl_2$ (25 mL) was refluxed for 4h. Excess $SOCl_2$ was removed in vacuo and then the crude acid chloride was combined with 2-azidoethanol (2.0 g, 23 mmol) in $ClCH_2CH_2Cl$ (25 mL). Dry pyridine (1.9 mL, 23 mmol) was added, and the entire mixture was stirred at r.t. for 2 days. The reaction mixture was washed with H_2O and $NaHCO_3$ (aq.), dried ($MgSO_4$) and concentrated in vacuo. Chromatography of the residue on silica gel eluting with petroleum ether/ethyl acetate (4:1) gave pure **8d** as a colorless clear oil (3.5g, 89%). IR(neat): 2100(s), 1728(s), 1312(s), 1277(m), 1237(m), 1207(m), 1180(s), 1101(w)cm^{-1}. ^{1}H NMR($CDCl_3$): δ 1.80, 1.96(ABq, J_{AB}=12.0Hz, 2H), 3.2~3.8(m, 10H), 4.27(t, J=4.8Hz, 4H)ppm. MS (CI/CH_4): *m/z* 373(M^++C_2H_5, 9), 345(M^++1, 26), 302(M^+–N_3, 11), 258 (M^+–$OCH_2CH_2N_3$, 100). Anal. Calcd. for $C_{15}H_{16}N_6O_4$: C, 52.32; H, 4.68; N, 24.41; Found: C, 52.15; H, 4.74; N, 24.22.

Pentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane-2,4-bis(1,3-diazidoisoproovlester) (**8e**)

8e was prepared in 84% yield as a colorless clear oil according to the procedure described for the preparation of **8d**. IR(neat): 2090(s), 1725(s), 1309(m), 1274(s), 1234(m), 1201(m), 1178(m), 1166(m), 1098(w)cm^{-1}. ^{1}H NMR($CDCl_3$): δ 1.80, 1.97(ABq, J_{AB}=12.2Hz, 2H), 3.2~3.9(m, 14H), 5.07(m, 2H) ppm. MS(EI): m/z 454(M^+, 7), 313(M^+–OCH(CH_2N_3)$_2$, 100). Anal. Calcd. for $C_{17}H_{18}N_{12}O_4$: C, 44.93; H, 3.99; N, 36.99; Found: C, 44.88; H, 4.09; N, 36.75.

Pentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane-2,4-bis(2,3-diazidopropylester) (8f)

8f was prepared in 85% yield as a colorless clear oil according to the procedure described for the preparation of **8d**. IR(neat): 2070(s), 1725(s), 1309(m), 1270(s), 1232(m), 1202(m), 1178(m), 1094(w)cm^{-1}. ^{1}H NMR($CDCl_3$): δ 1.82, 1.95(ABq, J_{AB}=12.0Hz, 2H), 3.3~3.9(m, 12H), 4.23(m, 4H)ppm. MS (CI/CH_4): m/z 483(M^++ C_2H_5, 7), 455(M^++1, 10), 412(M^+–N_3, 23), 313(M^+–$OCH_2CH(N_3)CH_2N_3$, 100). Anal. Calcd. for $C_{17}H_{18}N_{12}O_4$: C, 44.93; H, 3.99; N, 36.99; Found: C, 44.84; H, 4.02; N, 36.71.

ACKNOWLEDGMENT

We are grateful to Dr. Hong Yan for helpful discussions.

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