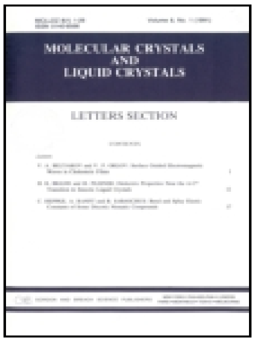


Taylor & Francis
Taylor & Francis Group

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Preparation, Characterization, and Molecular Structure of Two New Heat-Resistant Energetic Compounds

F. F. Chang, J. R. Zhang & R. F. Wu

To cite this article: F. F. Chang, J. R. Zhang & R. F. Wu (2015) Preparation, Characterization, and Molecular Structure of Two New Heat-Resistant Energetic Compounds, Molecular Crystals and Liquid Crystals, 623:1, 275-284, DOI: 10.1080/15421406.2015.1011457

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1011457

Mol. Cryst. Liq. Cryst., Vol. 623: pp. 275–284, 2015
Copyright © Inner Mongolia University of Technology
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1011457

Preparation, Characterization, and Molecular Structure of Two New Heat-Resistant Energetic Compounds

F. F. CHANG, J. R. ZHANG, AND R. F. WU*

Chemical Engineering College, Inner Mongolia University of Technology,
Hohhot, China

In this paper, nitration of 2,2′-diphenic acid was studied and two aromatic carboxylic acids containing two and four nitro groups, respectively, were synthesized and characterized through elemental analysis, IR spectra, respectively. Crystal structure of 4,4′-dinitro-2,2′-diphenic acid and 4,4′,6,6′-tetranitro-2,2′-diphenic acid was determined by X-ray single crystal diffraction and their thermal decomposition have been carried out through differential scanning calorimeter analyses at a heating rate of 10°C/min. The results indicate that the compounds have high heat-resistant stability.

Keywords Energetic compounds; molecular structure; thermal stability

Introduction

The nitration of deactivated aromatic compounds is an important reaction and plays a key role in the synthesis of medicines, pesticides, dyes, and explosives [1]. The DPA is a very good electron pair donor for two carboxyl groups, so it can be designed to assemble many novel metal-organic coordinate polymer materials (MOCP) with transition metal [2–5]. In order to explore the newly MOCP containing nitro groups for potential applications as heat-resistant energetic material, we decorated DPA by bringing more nitro groups to the aryl ring. In our previous study, nitration of 4,4′-biphenyl dicarboxylic acid have been reported [6, 7].

Herein, we report the nitration of DPA with high concentration sulfuric and nitric acids. The title molecules DNDPA and TNDPA containing two and four nitryls and two phenyls respectively, so their heating restrained stability and solubility will be improved so that they can be used as heating restrained energetic compounds and organic energetic ligands of MOCP materials.

In this work, we cultured single crystals of the two compounds in DMF. The molecular and crystal structures were determined by X-ray single-crystal diffraction analysis. The thermal decomposition processes of the compounds were investigated to examine their thermal stability.

---

*Address correspondence to R. F. Wu, Chemical Engineering College of Inner Mongolia University of Technology, Aimin Street No. 49, District of Xincheng, Hohhot, 010051, China. E-mail: rfwu02@imut.edu.cn

Experimental, Material, and Measurement

All analytical grade chemicals and solvents were purchased commercially and used without further purification. Elemental analysis was carried out on Carlo Erba 1106 full-automatic trace organic elemental analyzer. FT-IR spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer in dry KBr pellet in the range of 400–4000 cm^{-1}. A perkin-Elmer Pyris-1 differential scanning calorimeter (DSC) was used for DSC measurement (sample mass: about 1.0 mg, atmosphere: flowing nitrogen gas, reference sample: α-Al2O3, heating rate: 10°C/min).

X-Ray Crystallography

The data collections were performed on Rigaku AFC-10/Saturn 724 + CCD detector diffractometer equipped with a graphite-monochromatic MoK/α radiation ($\lambda = 0.71073$Å) at 153(2)K by using the ω scans with a multiscan mode. The structure was solved by direct methods using SHELXS-97 program [8] and refined by full-matrix least-squares methods on F2 with SHELXL-97 program [9].

Synthesis of DPA

Synthesis of DPA followed the literature [10]. A solution of phenanthrene (9 g) in 20 mL pyridine was stirred with 30 g potassium permanganate at 70°C and lasted half an hour. Then 30 mL sodium hydroxide was added into the solution and the reaction was continuously stirred until the purple disappeared completely. An amount of 50 mL distilled water was mixed into the solution when it was cooled. The pyridine was steamed out from the solution. The filtrate was acidified with hydrochloric acid and 7 g white crystal product obtained by filtration, the yield was 70%. mp: 231–232°C.

Synthesis of DNDPA

An amount of 12.1 g of DPA was dissolved in 75 mL of concentrated sulfuric acid and 25 mL fuming nitric acid was added into the solution keeping the temperature below 50°C. After addition, the solution was stirred continuously for 10 min, quickly heated to 60°C and then kept at this temperature for 2 hr. Consequently, the reaction mixture was poured into a little crushed ice. After several hours, the slightly yellow solid was collected on a filter, washed and dried at 60°C and 14.2 g of DNBPDC was obtained. mp: 236°C (decomposed). The product is insoluble in ether, chloroform, and cold water, but soluble in alcohol and DMF. When the material was recrystallized from DMF at high temperature, very fine needles were obtained. Anal. Calcd. (%) for C16H15N3O8: C, 50.93; H, 4.01; N, 11.14. Found (%): C, 50.90; H, 3.99 N, 11.05. IR: νas (CO_2–) 1709(s) cm^{-1}, νs (NO2)1344 (s) cm^{-1}, and νas (NO2) 1533(m) cm^{-1}.

Synthesis of TNDPA

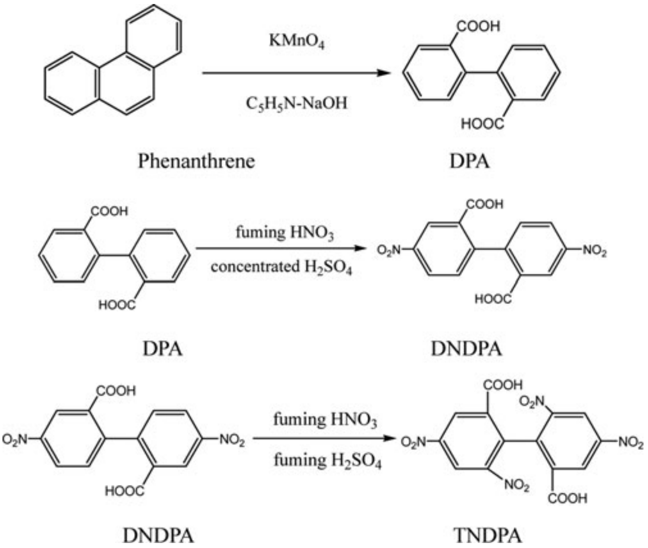
A solution of 16.6 g of DNDPA in 25 mL of fuming sulfuric acid was stirred and treated keeping the temperature bellowing 50°C with 8.4 mL fuming nitric acid. After the nitric acid has been added, the cooling bath was removed and the reaction mixture which is stirred continuously is allowed to warm to 90°C slowly. At the end of two hours, the clear solution is diluted with 40 g of ice and 40 mL of water and left in the ice box overnight.

By dissolving the crude product in hot water and cooling to room temperature, 18.8 g of TNBPDC was obtained after drying at 60°C. mp: 294°C (decomposed). When the product was recrystallized from DMF, very fine pale yellow needles were obtained. Anal. Calcd. (%) for C14H6N4O12: C, 39.83; H, 1.43; N, 13.27. Found (%): C, 39.81; H, 1.42; N, 13.23. IR: νas (CO_2–) 1716(s) cm^{-1}, νs (NO2)1345 (s) cm^{-1}, and νas(NO2) 1535(m) cm^{-1}.

Results and Discussion

Synthesis

The scheme 1 shows the equation of the synthesis of DNDPA and TNDPA. Similar to the synthesis of DNBPDC and TNBPDC [6, 7], DPA was subjected to a nitration reaction in the presence of mix acid [e.g., concentrated sulfuric acid and fuming nitric acid (DNDPA) or fuming sulfuric acid and fuming nitric acid (TNDPA)]. DPA nitration by mixed acid is a heterogeneous liquid–liquid reaction, which occurs almost exclusively in the aqueous phase. The organic compound diffuses into the aqueous mixed-acid-phase and reacts with the nitronium ion generated by the reaction between concentrated sulfuric acid and nitric acid.



Scheme 1. Procedure of preparing the two title compounds.

The crystal of DNDPA was obtained from DMF solution at high temperature, so the formyl group was removed from DMF molecule to form dimethylamine molecules, which coexist with DNDPA molecules in the unit cell.

Crystal Structure

The X-ray single-crystal structures of DNDPA and TNDPA were determined. The crystallographic data of the title compounds are listed in Table 1.

Table 1. Crystallographic data and structure refinement summary for the DNDPA and TNDPA

Compound	**DNDPA**	**TNDPA**
Empirical formula	$C_{16}\,H_{15}\,N_3\,O_8$	$C_{14}\,H_6\,N_4\,O_{12}$
Formula mass	377.31	422.23
Color, habit	Pale yellow, needle	Pale yellow, needle
Crystal dimensions (mm)	0.36 × 0.34 × 0.10	0.19 × 0.16 × 0.11
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/n
Z	8	4
a (Å)	7.559(2)	11.704(5)
b (Å)	10.228(3)	9.149(3)
c (Å)	44.390(13)	17.083(5)
β (°)	90.506(4)	116.69 (2)
Collection ranges	$-8 \le h \le -8; -12 \le k \le -12; -51 \le l \le 52$	$-13 \le h \le 13; -10 \le k \le 10; -11 \le l \le 20$
Temperature (K)	153(2)	153(2)
Volume (Å^3)	3431.8 (16)	1634.3(10)
Dcalcd (Mg/m^3)	1.461	1.716
Radiation	MoK_α ($\lambda = 0.71073$ Å)	Mo$K\alpha$ ($\lambda = 0.71073$ Å)
Absorption coefficient (mm^{-1})	0.119	0.155
Absorption correction	Multiscan	Multiscan
F(000)	1568	856
θ range for data collection (°)	2.04–25.00	2.50–25.00
Observed reflections	17,503	8,052
Independent eflections/R_{int}	5,800/0.0561	2,839/0.0448
Data/restraints/parameters	5,800/30/491	2,839/0/271
Goodness-of-fit on F^2	1.118	1.059
Final R indices [$I > 2\sigma(I)$]	0.1299/0.3164	0.0502/0.1091
R indices (all data)	0.1467/0.3264	0.0655/0.1191
Largest diff. peak and hole (e·Å^{-3})	0.586 and −0.577	0.244 and −0.302

DNDPA

As shown in Fig. 1, the unit cell contains two independent 4,4′-dinitro-2,2′-diphenic acid molecules and two dimethylamine molecules, which is similar to the molecule DPA [11] and DNBPDA [6]. The bond lengths and bond angles of two DNDPA molecules are different. A comparison of two DNDPA molecules reveals that the largest difference in distance is 0.025 Å, C(6)-C(7) and C(20)-C(21). Owing to the steric hindrance effect, the two aryl rings of the DNDPA are distorted with the torsion angle C(5)-C(6)-C(7)-C(8) of 49.36° and C(19)-C(20)-C(21)-C(22) of 46.81°. The planes of four carboxyl groups are also distorted with the aryl rings (torsion angle C(4)-C(5)-C(13)-O(4) = −155.4(8)°; C(7)-C(8)-C(14)-O(6) = −145.7(7)°; C(23)-C(22)-C(28)-O(13) = −146.1(8)°; and C(18)-C(19)-C(27)-O(12) = −142.7(7)°). One carboxyl group of each DNDPA molecules is deprotonated by dimethylamine molecules.

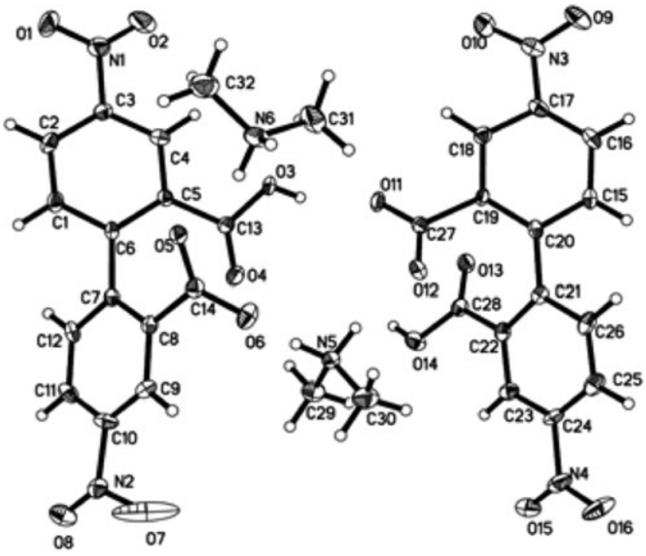


Figure 1. Molecular structure of the DNDPA.

Table 2. Select bond lengths/Å and bond angles/° for the compound DNDPA

	Dist	Angle	(°)
O(1)-N(1)	1.223(10)	O(2)-N(1)-O(1)	123.8(7)
O(2)-N(1)	1.209(10)	O(7)-N(2)-O(8)	120.7(7)
O(3)-C(13)	1.322(8)	O(4)-C(13)-O(3)	124.3(6)
O(4)-C(13)	1.190(8)	O(5)-C(14)-O(6)	125.9(6)
O(5)-C(14)	1.230(8)	O(10)-N(3)-O(9)	122.2(7)
O(6)-C(14)	1.263(8)	O(15)-N(4)-O(16)	124.0(7)
O(7)-N(2)	1.196(9)	O(12)-C(27)-O(11)	126.9(6)
O(8)-N(2)	1.199(9)	O(13)-C(28)-O(14)	123.5(6)

Table 3. Hydrogen bond lengths (Å) and angles (°) for DNDPA

No.	Donor–H . . . Acceptor	D–H	H . . . A	D . . . A	D–H . . . A
1	N(6)-H(6B) . . . O(5)#1	0.92	1.85	2.738(7)	160.3
2	N(6)-H(6A) . . . O(11)#2	0.92	1.92	2.778(8)	155.2
3	N(5)-H(5B) . . . O(12)	0.92	1.88	2.745(7)	154.9
4	N(5)-H(5A) . . . O(4)#1	0.92	2.57	3.073(7)	115.3
5	N(5)-H(5A) . . . O(6)#1	0.92	1.95	2.785(8)	150.6
6	O(14)-H(14O) . . . O(6)#3	0.84	1.74	2.518(7)	152.2
7	O(3)-H(3O) . . . O(11)#4	0.84	1.76	2.540(7)	154.0

Symmetry codes: #1: x,y+1,z; #2: x-1,y,z; #3: x+1,y+1,z; #4: x,y-1,z.

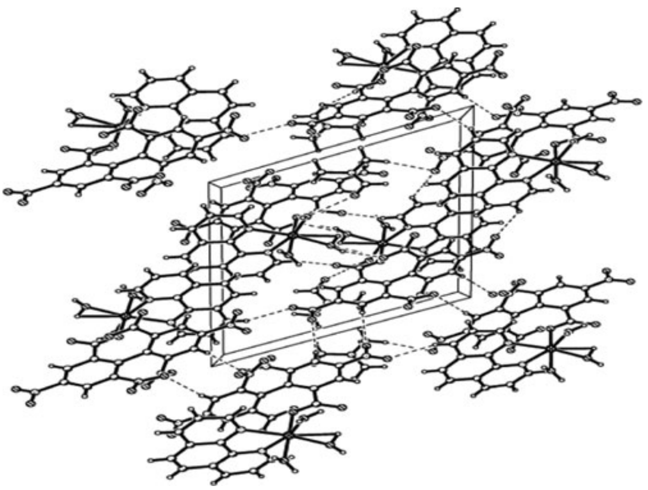


Figure 2. Crystal packing of the DNDPA.

Three nitro groups (1-NO2, 2-NO2, and 3-NO2) were split into two parts with 0.5 occupancy for obtaining good thermal parameters. The planes of these NO2 groups are distorted with the aryl ring. However, the 4-NO2 group is closely coplanar with the aryl ring. The N—O bond lengths in nitro groups are around the normal N—O double bond in nitro group (about 1.200 Å) (Table 2) [12]. The C=O bond lengths of carboxyl groups varied from 1.200(9) Å to 1.262(9) Å. However, the C—O (H) bond lengths of carboxyl groups change from 1.323(9) Å to 1.331(9) Å, which is evidently shorter than that of the free carboxyl groups (1.41–1.44 Å).

In the molecule DNDPA, two aryl rings of biphenyl which come from two molecules stack offset face-to-face in infinite columns along a which are linked into layers and the distance of two planes is 3.611 Å ($\theta = 20.53°$), which is in the range of π–π stacking interaction (3.3–3.7 Å) [12]. So there are existence of π–π stacking interaction that benefits for the formation and stability of the crystals. These layers are held together via

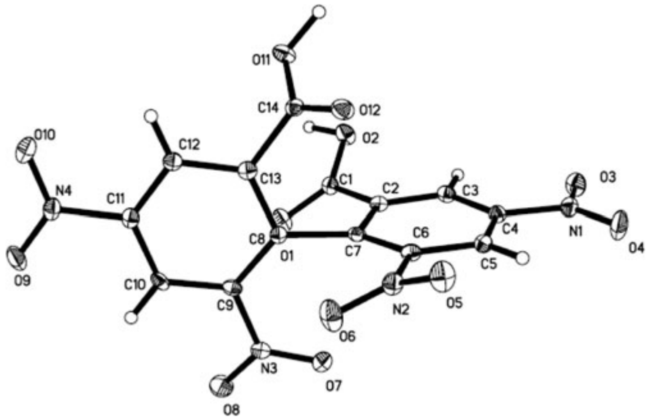


Figure 3. Molecular structure of the TNDPA.

Table 4. Select bond lengths/Å and bond angles/° for the compound TNDPA

	Dist	Bond	Dist	Angle	(°)
O(1)-C(1)	1.228(3)	O(5)-N(2)	1.225(3)	O(3)-N(1)-O(4)	124.5(2)
O(2)-C(1)	1.299(3)	O(6)-N(2)	1.216(3)	O(6)-N(2)-O(5)	125.0(2)
O(11)-C(14)	1.294(3)	O(7)-N(3)	1.215(3)	O(7)-N(3)-O(8)	124.2(2)
O(12)-C(14)	1.234(3)	O(8)-N(3)	1.221(3)	O(9)-N(4)-O(10)	124.3(2)
O(3)-N(1)	1.222(3)	O(9)-N(4)	1.216(3)	O(1)-C(1)-O(2)	124.6(2)
O(4)-N(1)	1.223(3)	O(10)-N(4)	1.220(3)	O(12)-C(14)-O(11)	125.0(2)

intermolecular hydrogen bonds. The nitrogen atoms of two dimethylamine molecules [N(6) and N(5)] are involved in an intricate hydrogen bonding network as well as the oxygen atoms [O(5), O(11), O(12), O(4), and O(6)] of carboxyl group (Table 3). In particular, the strongest hydrogen bonding interactions are O(14) and O(3) [carboxyl oxygen atoms: O(14)... O(6)#3 2.518(7) Å(#3 $x+1,y+1,z$); O(3)... O(11)#4 2.540(7) Å(#4 $x,y-1,z$)]. Thus a 2D infinite layer structure is formed through π–π stacking interaction along a direction and intermolecular hydrogen bonds alone c direction (Fig. 2).

TNDPA

The building unit of the TNDPA is composed of a 4,4′,6,6′-tetra nitro-2,2′-biphenyl dicarboxylic acid molecules (Fig. 3). The two aryl rings of the TNDPA molecule are close to vertical (the torsion angle: C(2)-C(7)-C(8)-C(9) is 90.48°). Same as the DNDPA, the carboxyl groups of the TNDPA are not coplanar with the aryl rings because of steric hindrance effect. The C=O bond lengths of carboxyl groups varied from 1.228(3) Å to 1.234(3) Å and the C—O (H) bond lengths of carboxyl groups change from 1.294(3) Å to 1.299(3) Å (Table 4), which are in the normal range of C=O and C—O(H) bond lengths of the carboxyl group [12].

The 4-NO2 and 4′-NO2 are close to coplanar with the aryl rings (torsion angles: O(10)-N(4)-C(11)-C(10) −178.8(2)°; O(4)-N(1)-C(4)-C(3) 179.6(2)°), but 2-NO2 and 2′-NO2 are distorted because of steric hindrance effect (torsion angles: O(7)-N(3)-C(9)-C(10) −169.7(2)°; O(6)-N(2)-C(6)-C(5) −156.9(2)°).

The TNDPA molecules is linked to a 1D infinite chain structure through two intermolecule hydrogen bonds which are formed between a O—H group and an oxygen atoms of carboxyl group (Table 5). As shown in Fig. 3, owing the two aryl rings of biphenyl are vertical, two adjacent TNDPA molecules staggered arrangement. So two adjacent 1D arrays are extended to a 2D framework (Fig. 4).

Table 5. Hydrogen bond lengths (Å) and angles (°) for TNDPA

No.	Donor–H... Acceptor	D–H	H... A	D... A	D–H... A
1	O(2)-H(2)... O(12)#1	1.05	1.55	2.594(3)	170.8
2	O(11)-H(11)... O1#2	1.03	1.58	2.592(3)	167.0

Symmetry codes: #1: $-x+1,y+1/2,-z+3/2$; #2: $-x+1,y-1/2,-z+3/2$.

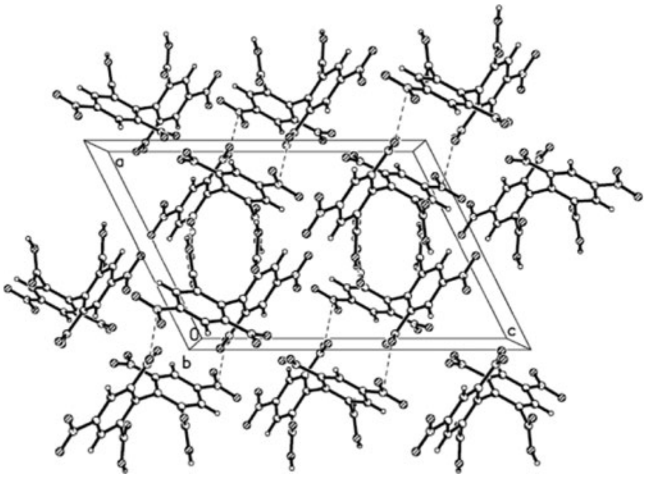


Figure 4. Crystal packing of the TNDPA.

Thermal Behavior

The DSC curves of the title compounds shown in Figs. 5 and 6, respectively, indicate the decomposition occurs in the 50°C–600°C range. In Fig. 5, there is one exothermic process at 20–350°C range with the peak at 239°C and two endothermic process at 320–650°C with the peak at 373°C and 568°C. In Fig. 6, there is only one aculeate endothermic with the peak at 331°C. From the result, we find that the compound TNDPA have four nitro groups in aromatic rings, so initial decomposition temperature of endothermic process is lower than the compound DNDPA that has two nitro groups. However, the compound DNDPA and TNDPA both have higher initial decomposition temperatures (above 200°C).

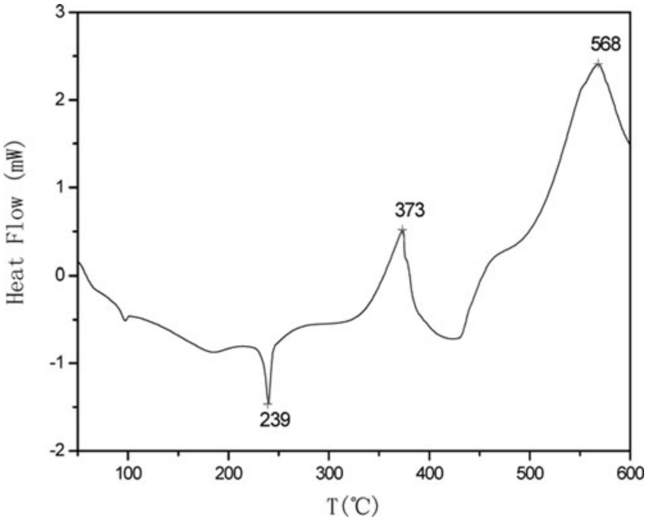


Figure 5. The DSC for DNDPA.

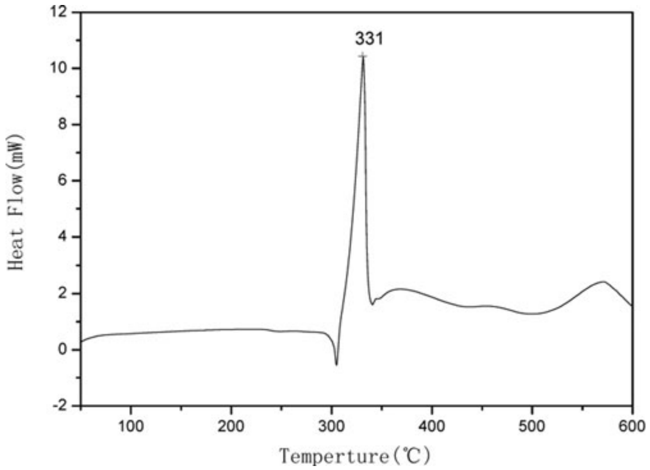


Figure 6. The DSC for TNDPA.

Conclusion

In summary, we have successfully synthesized two aromatic carboxylic acid compounds containing two and four nitro groups, respectively, by nitration of DPA with mixed sulfuric and nitric acids. Single crystals of the title compounds were grown using solution growth technique. X-ray single-crystal analysis revealed that the nitro-substitution of the compound DNDPA and TNDPA occurs on 4,4′ positions and 4,4′,6,6′ positions, respectively. The structure of the compound DNDPA is a 2D-layered structure by π–π stacking interaction and intermolecular hydrogen bonds. The compound TNDPA also is a 2D-layered structure by intermolecular hydrogen bonds. The functional group was confirmed by element analysis and FT-IR. The thermodynamic analysis result indicates the title compounds have higher thermal stability although it contain two and four nitryls and can be used as heating restrained energetic compound or organic energetic ligands of MOCP materials.

Supplementary Data

Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Center, CCDC reference number 1016480 and 1016481 for DNDPA and TNDPA, respectively. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: t44-1223 336-033; Email: deposit@ccdc.cam.ac.uk).

Funding

This paper was supported by the National Natural Science Foundation of China (21164005) and the Natural Science Foundation of Inner Mongolia (2010MS0212).

References

[1] Olah, G. A., Malhotra, R., & Narang, S. C. (1989). *Nitration Methods and Mechanisms*, VCH Publications: Germany.

[2] Wang, R. H., Han, L., Lin, Z. Z., Luo, J. H., & Hong, M. C. (2004). *Chin. J. Struct. Chem.*, *23*, 403–406.

[3] Rueff, J. M., *et al.* (2002). *Eur. J. Inorg. Chem.*, *4*, 895–900.

[4] Lu, J. Y., & Schauss, V. (2003). *Chem. Commun.*, *6*, 1332–1334.

[5] Li, X. M., Wang, Q. W., & Liu, B. (2011). *Chin. J. Struct. Chem.*, *30*, 1464–1468.

[6] Wu, R. F., Zhang, T. L., & Qiao, X. J. (2010). *Chin. Chem. Lett.*, *21*, 1007–1010.

[7] Wu, R. F., Shi, H. P., & Zhang, T. L.(2011). *Chin. J. Struct. Chem.*, *6*, 877–881.

[8] Sheldrick, G. M. (1997). *SHELXS 97, Program for the Solution of Crystal Structure*, University of Göttingen: Germany.

[9] Sheldrick, G. M. (1997). *SHELXS 97, Program for the Refinement of Crystal Structures*, University of Göttingen: Germany.

[10] Yao, M. Z., & Li, Y. S. (1988). *J. Dallan Inst. Technol.*, *27*, 73–78.

[11] Fronczek, F. R., Davis, S. T., Gehring, L. M. B., & Gandour, R. D. (1987). *Acta Crystallogr. Sect. C.*, *43*, 1615.

[12] Chen, X. M., & Cai, J. W. (2003). *Crystal Structure Analysis*, Science Publisher; America.