Article

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A New, Fast and Easy Strategy for One-pot Synthesis of Full Substituted Cyclopropanes: Direct Transformation of Aldehydes to 3-Aryl-1,1,2,2-tetracyanocyclopropanes

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A new, fast and easy method for one-pot reaction of aromatic aldehydes and dialdehydes with malononitrile and cyanogen bromide has been developed to afford full substituted 3-arylcyclopropane-1,1,2,2-tetracarbonitriles in excellent yields in very short time (about 5 seconds). The structures elucidations were characterized by IR, ^{1}H NMR, ^{13}C NMR, mass spectrometry and X-ray crystallography techniques. For these compounds the crystallographic data showed two structures in mirror image in solid case and one distinct structure in solution. The reaction mechanism was discussed.

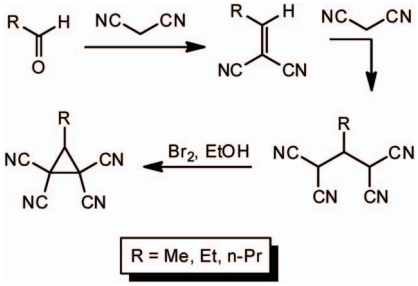
Keywords: Malononitrile; One-pot reaction; Tetracyanopropanes; Cyanogen bromide.

INTRODUCTION

In multicomponent reactions (MCRs), three or more reactants come together in a single reaction vessel to form new products that contain structural unit so fall the components. This type of reaction becomes increasingly important in organic and medicinal chemistry because it allows to obtain highly sophisticated polyfunctional molecules through simple one-pot procedures. Multicomponent reactions have been successfully employed to generate highly diverse combinatorial libraries for high-throughput screening of biological and pharmacological activities. By using of three or more building blocks in a one-pot, a high yielding multicomponent reaction leads to a wide structural and functional diversity combined with excellent combinatorial efficiency. Over the past decade, industrial and academic research has made powerful MCRs strategies into one of the most efficient and cost-effective tools for combinatorial synthesis.[1,2] The development of novel MCRs is an intellectually challenging task since one has to consider not only the reactivity match of the starting materials but also the reactivity of the intermediate molecules generated in situ, their compatibility and their compartmentalization.[3]

The cyclopropyl group is an important structural motif in many herbal compounds, displaying antibacterial, antiviral and some enzyme inhibition activities.[4-6] First synthesis of 3-substituted cyclopropane was described by Mariella *et al.* [7] (Scheme I). In this reaction, at first the simple condensation reaction of aldehyde and malononitrile affordes alkylidenemalononitriles then reaction with the second malononitrile affords Michael adduct. Then bromination of this product with bromine is done, and finally intramolecular nucleophilic attack of carbon atom to the other carbon containing bromine atom (pushing the bromide ion out) produces 3-substituted cyclopropane.[7]

Scheme I Synthesis of 3-alkylcyclopropane-1,1,2,2-tetracarbonitrile in the reaction with bromine[7]



The methods of cyclopropane synthesis have been divided into two main groups: namely intramolecular cyclization and addition between alkenes and carbenes.[4,6] On the other hand, Michael Initiated Ring Closer (MIRC) is an important synthetic method for cyclization.[5] Reaction of halogenated acid anion with the activated alkene followed by cyclization along with elimination of halogen has generated tetramethyl 3,3-dialkylcyclopropane-1,1,2,2-tetracarboxylates (full substituted cyclopropanes)[6] (Scheme II).

The use of alkylidenemalononitriles is common in organic synthesis. Direct transformation of benzylidenemalononitriles and malononitrile into 3-aryl-1,1,2,2-tetracy-

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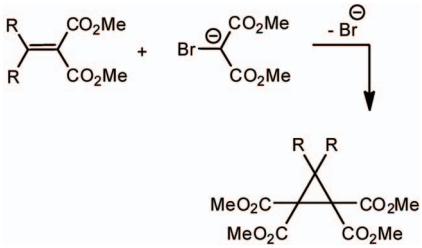
Scheme II Synthesis of tetramethyl 3,3-dialkylcyclopropane-1,1,2,2-tetracarboxylates[6]



anocyclopropanes in basic alcohol solution has been described by Elinson *et al.*[8] On the other hand, one-pot cascade assembling of 3-substituted tetracyanocyclopropanes from alkylidenemalononitriles and malononitrile by the only bromine direct reaction has also been reported by the same group.[9,10]

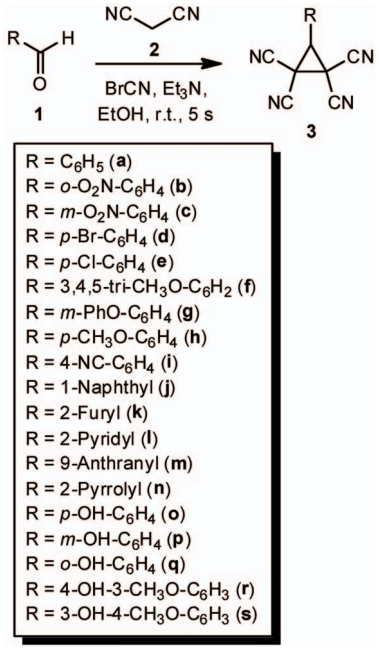
Cyanogen bromide is a toxic but very useful reagent in organic synthesis.[11,12] It is a capable reagent for the synthesis of cyanamides,[11] cyanates,[12] and also used to selective cleavage of the methionyl peptide bonds in ribonuclease[13] and etc. Furthermore this compound is a useful brominating and cyanating agent for the bromination and cyanation of imidazoles,[14] free radical reaction with alkanes that results in bromination of alkanes[15] and α-bromination of β-aminoenones.[16] More recently, we have reported the reaction of (thio)barbituric acids (as a symmetrical barbituric acids) with aldehydes[17] and ketones[18] in the presence of cyanogen bromide and triethylamine. Based on these concepts, we have accomplished a new and a very fast one-pot transformation of aldehydes and malononitrile to 3-arylcyclopropane-1,1,2,2-tetracarbonitriles in the presence of cyanogen bromide and triethylamine in excellent yields in a few seconds.

RESULTS AND DISCUSSION

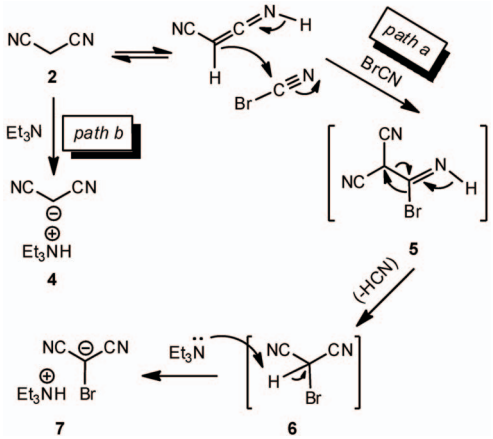
This paper describes a new route one-pot reaction of aldehydes (**1a-1l**) with malononitrile (**2**) and cyanogen bromide into 3-arylcyclopropane-1,1,2,2-tetracarbonitriles (**3a-3l**) in the presence of triethylamine in excellent yields in very short time (5 seconds) (Scheme III).

As described in Scheme IV, in these reactions, the in situ generated salt triethylammonium bromodicyanomethanide (**7**) plays an essential role for the synthesis of **3**. Proposed reaction mechanism for the formation of **7** is shown in Scheme IV. According to our search, there is no report about this compound in literature. The salt of **7** was isolated and characterized by spectroscopy techniques. The IR

Scheme III Synthesis of 3-arylcyclopropane-1,1,2,2-tetracarbonitriles (**3**) in the reaction of aldehydes (**1**) with malononitrile (**2**) in the presence of cyanogen bromide and triethylamine



Scheme IV Proposed mechanism for the synthesis of **7**



spectrum of **7** shows the frequency of NH^+ stretching at the broad range of 2500-3300 cm^{-1}, frequency of CN and C-Br stretching at 2167 and 565 cm^{-1}, respectively. The ^1H NMR spectrum of this compound shows (integration in parenthesis) a triplet at δ 1.39 (9H) and a multiplet (a quartet approximately) at δ 3.14 ppm (6H) are corresponding to methyl and methylene protons in triethylammonium salt

moiety, respectively. A broad singlet at δ 9.78 ppm (1H) is of NH^+ in this salt. ^{13}C NMR spectrum of this salt shows four distinct peaks that confirm the structure of **7** (Fig. 1 and see supplementary data). Unfortunately, all attempts failed to separate or characterize intermediates **5** and **6**. Other evidence for the formation and confirmation of **7** (the existence of bromine atom in this salt structure) was performed by Beilstein test and the wet silver nitrate test (precipitate of pale yellow silver bromide). On the basis of the well established chemistry of barbituric acids in the reaction with cyanogen bromide in the presence of triethylamine[17,18] and also the mechanism of the bromination of imidazoles by cyanogen bromide,[14] it is reasonable to assume that the compound **2** reacts directly with cyanogen bromide to form 2,2-dicyanoacetimidoyl bromide (**5**) intermediate through path *a*. Intramolecular rearrangement of this intermediate produces 2-bromomalononitrile (**6**) intermediate. Finally, triethylamine as a base captures the acidic proton to afford **7** (Scheme IV). Malononitrile **2** directly reacts with triethylamine to form the salt of triethylammonium dicyanomethanide (**4**) in the absence of cyanogen bromide (path *b*). The salt of **4** was also separated and characterized in direct reaction of **2** with triethylamine through path *b* (see experimental and Scheme IV). We performed the reaction of **2** with cyanogen bromide in the presence of triethylamine and in the absence of aldehydes, **1** so the compound **7** was isolated in excellent yield. On the other hand, in the presence of aldehyde, compounds **3** and **7** were isolated as major and minor products, respectively. These experiments confirm the major role of **7** in the synthesis of **3**.

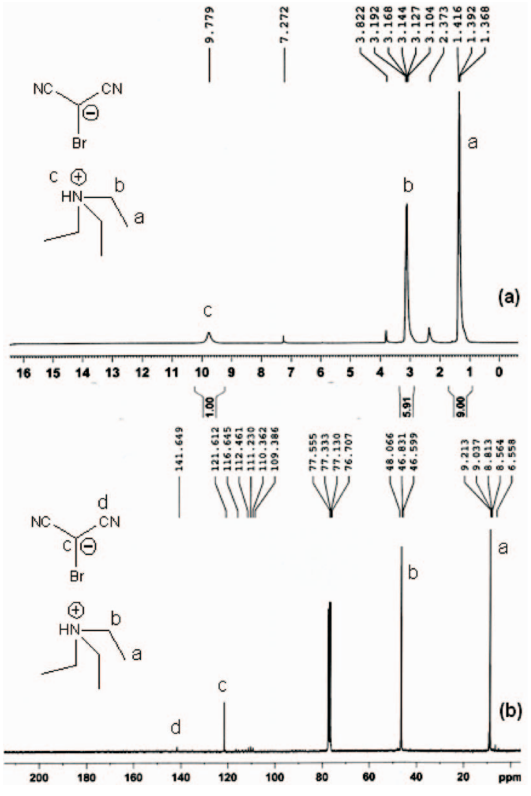


Fig. 1. Characterized ^1H (a) and ^{13}C NMR (b) spectra of **7**.

Another evidences for the confirmation of **7** is the formation of reported salts of triethylammonium-5-bromo (thio)barbiturates (**13a′-13c′**).[17,18] Representatively, the reaction of **2** with cyanogen bromide in the presence of triethylamine in ethanol afforded the salt of **7** as we have described recently the reaction mechanism in the case of (thio)barbituric acid (**11a′-11c′**),[17-20] 5,5-dimethylcyclohexane-1,3-dione (dimedone, **12a′**) and 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid, **12b′**). Similarly, the reaction of **11a′-11c′**, **12a′** and **12b′** with BrCN afforded the corresponding salts of **13a′-13c′**,[17,18] triethylammonium 1-bromo-4,4-dimethyl-2,6-dioxocyclohexan-1-ide (**14a′**) and triethylammonium 5-bromo-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide (**14b′**) in the presence of triethylamine at the range of 0 °C to room temperature (Fig. 2).

Representatively, the reaction mechanism for the formation of **3e** is shown in Scheme V. First, the reaction of al-

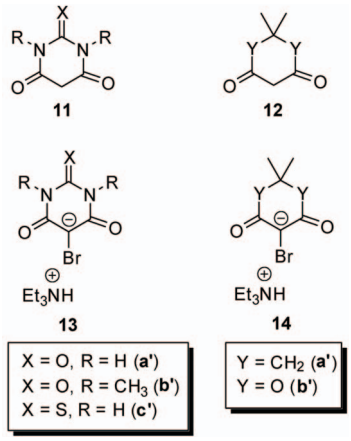
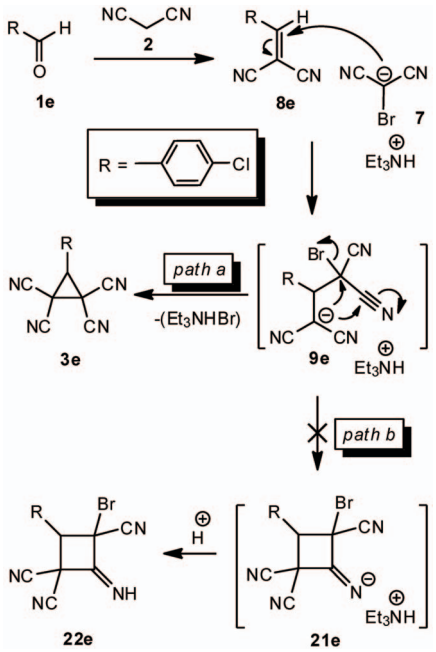


Fig. 2. Formula structures of (thio)barbituric acids (**11a′-11c′**), dimedone (**12a′**), Meldrum's acid (**12b′**), triethylammonium-5-bromo (thio)barbiturates (**13a′-13c′**),[17,18] triethylammonium 1-bromo-4,4-dimethyl-2,6-dioxocyclohexan-1-ide (**14a′**) and triethylammonium 5-bromo-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide (**14b′**).

Scheme V Representatively, proposed mechanism for the synthesis of **3e** (path *a*) and no path *b* was occurred



dehyde **1e** with malononitrile **2** was afforded 2-(4-chlorobenzylidene)malononitrile (**8e**) then the nucleophilic attacking of **7** to the β-carbon position of **8e** as an α,β-unsaturated compound afforded intermediate triethylammonium 3-bromo-2-(4-chlorophenyl)-1,1,3,3-tetracyanopropan-1-ide (**9e**). Intramolecular *C*-attack of carbanion to carbon atom containing bromine atom (path *a*) as an electrophile (pushing the bromide ion out) produced 3-(4-chlorophenyl)cyclopropane-1,1,2,2-tetracarbonitrile (**3e**). All attempts to separate and characterize the intermediates **8** and **9** failed. No **22e** was observed through intermediate **21e**. This observation indicated that the *C*-attack of carbanion to nitrile group did not occur (Scheme V, path *b*).

Representatively, the reaction of **1e** and **2** exclusively were obtained **8e** in the presence of triethylamine and absence of cyanogen bromide. It has been shown that the salt of **7** plays the major role in these reactions. First, it is a nucleophile in the reaction with **8e** then it has an electrophilic character (carbon atom containing of bromine) in the intermediate **9e** to form **3e** (Scheme V). The reaction condition, time and yields are outlined in Table 1.

Representatively, ^{1}H NMR spectrum of **3e** show a singlet at δ 5.03 ppm corresponding to cyclopropyl C-H proton and two doublets at δ 7.63 and 7.95 ppm (J = 8.4 Hz) for 4-chlorophenyl ring. ^{13}C NMR spectrum of this compound shows eight distinct peaks. The peaks at δ 108.9 and 110.4 ppm corresponds to the cyano groups with different chemical shifts. The IR spectrum shows two peaks at the frequency of 2264 and 2211 cm^{-1} that confirms the existence of cyano groups in the molecule. These data are in good agreement together with the formula structure of **3e** as representative (see experimental section and supplementary data).

The reaction of bulky aldehyde such as 9-anthracene carbaldehyde (**1m**) and aldehydes containing exchangeable protons such as 2-pyrrole carbaldehyde (**1n**) and containing hydroxyl group (**1o-1s**) with **2** and BrCN in the presence of triethylamine afforded Knoevenagel adducts (**8m-8s**) and did not match cyclopropane products (**3m-s**). Presumably, the hindrance effect in **1m** led to formation of **8m**. Instead, the existence of acidic NH group on **8n** and OH group upon **8o-8s**, caused the **7** as nucleophile to be able to capture acidic proton on NH and/or OH group (path *a*) prior to Michael addition to β-carbon position of Knoevenagel adducts **8n-8s** (path *b*) (Scheme VI). Therefore, the path *a* is favored than that of path *b*. It seems that the existence of exchangeable proton having acidic nature

Scheme VI Proposed mechanism for the favoring of path *a* and unfavored path *b*

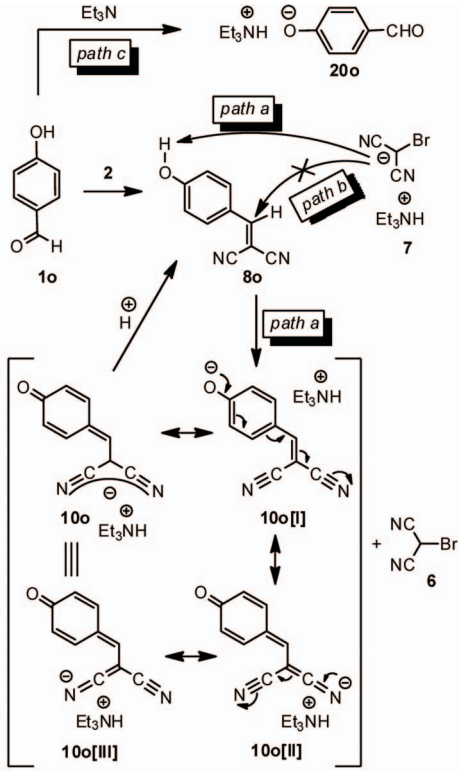
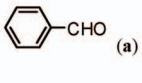
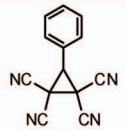
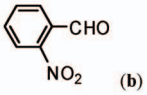
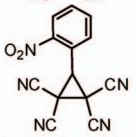
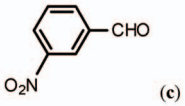
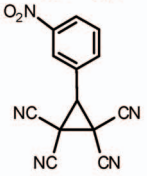
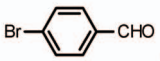
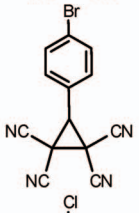
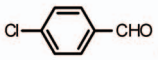
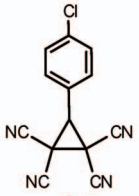
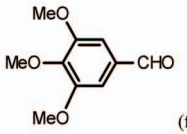
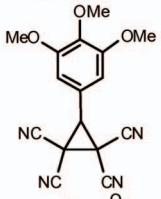
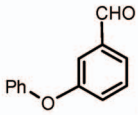
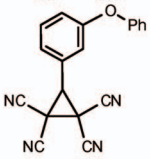
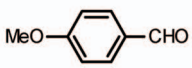
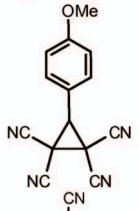
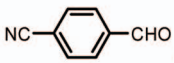
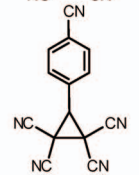
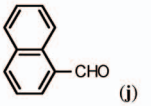
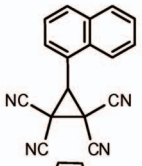
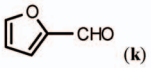
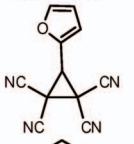
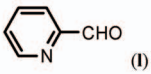
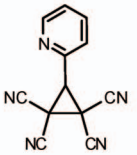
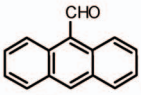
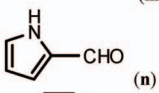
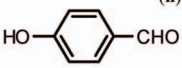
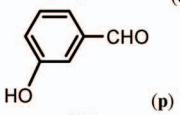
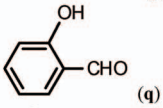
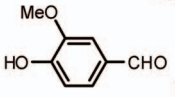
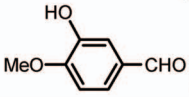


Table 1. The structure of reactants (**1**), products (**3**) and reaction time and yields

Entry	Aldehyde (Reactant **1**)	Product (**3**)	Reaction time (sec.), Yield (%)[a]
1	 (**a**)		5, 100
2	 (**b**)		5, 100
3	 (**c**)		5, 100
4	 (**d**)		5, 100
5	 (**e**)		5, 100
6	 (**f**)		5, 90
7	 (**g**)		5, 90
8	 (**h**)		5, 95
9	 (**i**)		5, 100
10	 (**j**)		5, 95
11	 (**k**)		5, 90
12	 (**l**)		5, 90
13	 (**m**)	-[b]	80[c]
14	 (**n**)	-[b]	[d]
15	 (**o**)	-[b]	75[c]
16	 (**p**)	-[b]	77[c]
17	 (**q**)	-[b]	75[c]
18	 (**r**)	-[b]	80[c]
19	 (**s**)	-[b]	80[c]

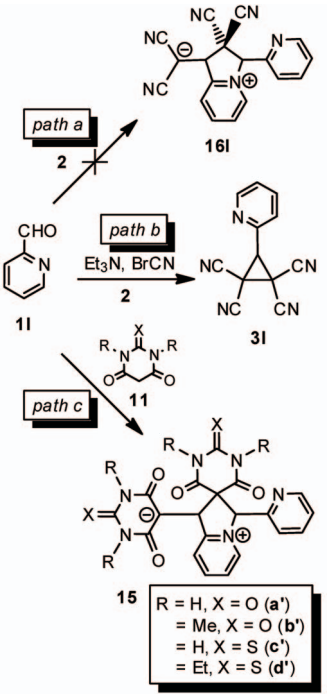
[a] Yield refer to isolated product. [b] Knoevenagel adducts were obtained. [c] Yield of conversion to Knoevenagel adducts. [d] Unknown black viscous tar was obtained.

on Knoevenagel adducts prevented the Michael addition of **7** and made the path *a* more favorable (Scheme VI). Another possible pathway can be path *c*. Triethylamine as a base can attack to acidic proton on phenol derivative (4-hydroxy benzaldehyde **1o** as representative) to form triethylammonium 4-formylphenolate **20o** (Scheme VI, path *c*). Our attempt to separate and characterize **8o**, **10o** and **20o** failed. These results demonstrated the reason of unsuccessful cyclopropanation of aromatic aldehydes possessing exchangeable proton.

The reaction of picolinaldehyde (**1l**) with some β-dicarbonyl compounds such as 1,3-dialkylated (thio)barbitu-

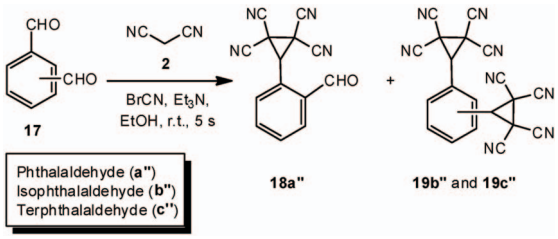
ric acids (For instance **11a′-d′**) was exclusively afforded zwitterionic salts of (thio)barbiturates (**15b′**)[21] and (**15a′-d′**)[22] (Scheme VII, path *c*). Based on this concept, our aim was an attempt for synthesis of the zwitterionic salt of dicyano (2,2-dicyano-3-(pyridin-2-yl)-2,3-dihydro-1*H*-indolizin-4-ium-1-yl)methanide (**16l**) in the reaction of **1l** with **2** under natural condition and no **16l** was observed (path *a*). In this current reaction, **3l** was obtained in the presence of BrCN and triethylamine in excellent yield (Scheme VII, path *b*).

Scheme VII Reaction of picolinaldehyde (**1l**) with malononitrile (**2**) for synthesis of **3l** in the presence of Et_3N. An attempt for synthesis of zwiterionic salt of **16l** under natural condition was unsuccessful



We also performed the reaction of phthalaldehyde (**17a″**), isophthalaldehyde (**17b″**) and terphthalaldehyde (**17c″**) with **2** in the presence of cyanogen bromide and triethylamine under the same condition (Scheme VIII). The reaction of **17a″** with **2** and cyanogen bromide in the presence of triethylamine was afforded 3-(2-formylphenyl)cyclopropane-1,1,2,2-tetracarbonitrile (**18a″**) due to *ortho* hindrance effect. In respect to the **17b″** and **17c″**, both aldehyde groups in each compound were reacted with **2** and were obtained 3,3′-(1,3-phenylene)bis(cyclopropane-1,1,2,2-tetracarbonitrile) (**19b″**) and 3,3′-(1,4-phenylene)bis(cyclopropane-1,1,2,2-tetracarbonitrile) (**19c″**), respectively. The reaction condition and yields of aromatic dialdehydes **17a″-17c″** are outlined in Table 2.

Scheme VIII Reaction of phthalaldehyde (**17a″**), isophthalaldehyde (**17b″**) and terphthalaldehyde (**17c″**) with **2** in the presence of cyanogen bromide and triethylamine



Representatively, ^{1}H NMR spectrum of **18a″** show a singlet at δ 5.08 ppm corresponding to cyclopropyl C-H proton and three multiplets at δ 7.95, 8.20 and 8.30 ppm for phenyl ring and a singlet at δ 10.27 corresponds to aldehyde proton. ^{13}C NMR spectrum of this compound shows

Table 2. The structure of dialdehydes (**17**), products (**18** and **19**) and reaction time and yields

Entry	Dialdehyde (**17**)	Product (**18** and/or **19**)	Reaction time (sec.), Yield (%)[a]
1	(a")	(18a")	5, 95
2	(b")	(19b")	5, 95
3	(c")	(19c")	5, 83[b]

[a] Yield refer to isolated product. [b] The **18c″** (≈7%) and unknown compound (≈10%) was also obtained.

eleven distinct peaks. The peaks at δ 109.2 and 110.7 ppm corresponds to the cyano groups with different chemical shifts and a peak at 193.8 related to carbonyl group. The IR spectrum shows two peaks at the frequency of 2259 and 1682 cm^{-1} that confirms the existence of cyano and carbonyl groups in the molecule. The ^{1}H NMR spectrum of **19b″** show a singlet at δ 5.24 ppm, a triplet at δ 7.81 (J = 8.1 Hz), a doublet at δ 8.14 (J = 7.8 Hz) and a singlet at δ 8.44 ppm corresponding to cyclopropyl C-H and phenyl protons, respectively. ^{13}C NMR spectrum of this compound shows eight distinct peaks. IR spectrum show a distinct peak at the frequency of 2262 cm^{-1} and no carbonyl frequency absorption was observed in the IR spectrum. These data are in good agreement together with the formula structure of the **18a″** and **19b″**, respectively (see experimental section and supplementary data). In the reaction of terphthalaldehyde **17c″**, the **18c″** (≈7%) an unknown compound (≈10%) was also obtained. Attempt for the separation of **18c″** and unknown compound was unsuccessful due to their equal polarity.

Representatively, for further study of compound **3b**, an X-ray diffraction analysis of **3b** was undertaken. The results of this study confirmed unambiguously the proposed structure (Fig. 3). The crystal packing diagram of **3b** is shown in Fig. 4. The selected crystal data, bond lengths, angles and torsion angles are summarized in Tables 3 and 4, respectively. For the crystal structure determination, the single-crystal of the compound **3b** was used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). The graphite-monochromatized Mo K_α radiation (λ = 0.71073 Å) and oscillation scans technique with Δω = 5° for one image were used for data collection. The lattice parameters were determined by the least-squares methods on the basis of all reflections with $F^2 > 2\sigma(F^2)$. Integration of

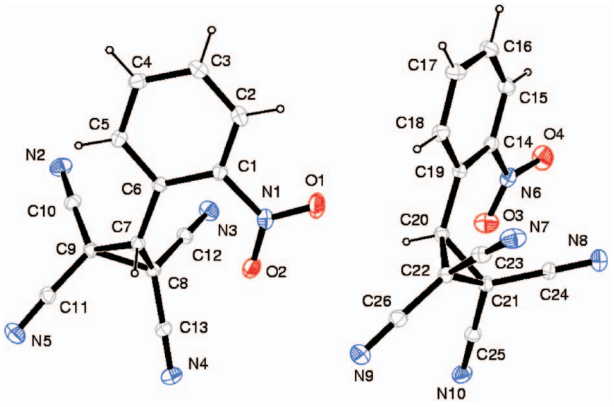


Fig. 3. ORTEP drawing of the compound **3b**. The asymmetric unit contains two isomers in mirror image. Thermal ellipsoids are shown at 30% probability level.

Table 3. Selected crystallographic data for **3b**

Crystal data (**3b**)	
Emprical Formula	$C_{13}H_5N_5O_2$
M	263.22
T(K)	293
Space group	$P2_1/c$
Crystal system	Monoclinic
a (Å)	13.8529 (2)
b (Å)	12.2866 (5)
c (Å)	14.1879 (4)
α (°)	90
β (°)	90.415 (3)
γ (°)	90
V (Å^3)	2414.79 (12)
Z	8
F(000)	1072
D_x (mg m^{-3})	1.448
λ (Å)	0.71073 Å
μ (mm^{-1})	0.105
Data collection	
R_{int}	0.116
θ_{max}, θ_{min}(°)	26.5/ 2.2
Refinement	
$R[F^2 > 2\sigma(F^2)]$	0.0752
$wR(F^2)$	0.236
S	0.976
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.19, –0.25

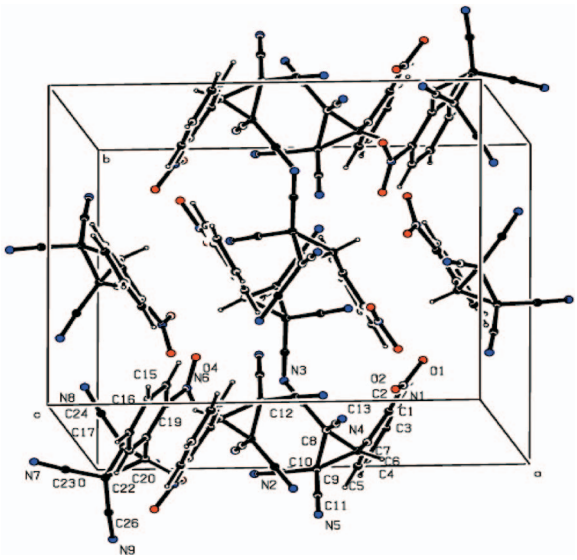


Fig. 4. Packing diagram of the compound **3b**.

Table 4. Selected bond length (Å), angles (θ, °) and torsion angles (φ, °) for **3b**

Atom	Bond length (Å), angles (θ, °) and torsion angles (φ, °)
C8—C9	1.556 (6)
C22—C21	1.561 (6)
N6—O4	1.210 (5)
N1—O1	1.216 (5)
C6—C7	1.492 (6)
C20—C19	1.496 (6)
C26—N9	1.139 (6)
N5—C11	1.142 (6)
C7—H7	0.9800
C20—H20	0.9800
C13—C8—C12	115.1 (4)
C25—C21—C24	114.2 (4)
C6—C7—C9	121.6 (4)
C19—C20—C22	121.6 (4)
C1—C6—C7	123.8 (4)
C14—C19—C20	124.6 (4)
O4—N6—O3	122.2 (5)
O2—N1—O1	122.4 (5)
N7—C23—C22	176.8 (6)
N2—C10—C9	176.7 (5)
O1—N1—C1—C2	2.6 (6)
O4—N6—C14—C15	14.2 (6)
C21—C20—C19—C14	61.8 (6)
C1—C6—C7—C8	–68.6 (6)
C13—C8—C9—C11	–0.4 (6)
C26—C22—C21—C25	–1.2 (6)

the intensities, correction for Lorentz and polarization effects and cell refinement was performed using CrystalClear (Rigaku/MSC Inc., 2005) software.[23] The structures were solved by direct methods using *SHELXS-97*[24] and refined by a full-matrix least-squares procedure using the program *SHELXL-97*.[24] H-atoms were positioned geometrically and refined using a riding model. The final difference Fourier maps showed no peaks of chemical significance. Crystallographic data were deposited in CSD under CCDC-871192 registration number. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/ data_request/cif and are available free of charge upon request to CCDC, 12 Union Road, Cambridge, UK (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk).

EXPERIMENTAL

General

The drawing and nomenclature of compounds were done by ChemBioDraw Ultra 12.0 version software. Melting points were measured with a digital melting point apparatus (Electrothermal) and were uncorrected. IR spectra were determined in the region 4000-400 cm^{-1} on a NEXUS 670 FT IR spectrometer by preparing KBr pellets. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker 300 FT-NMR at 300 and 75 MHz, respectively (Urmia University, Urmia, Iran). ^{1}H and ^{13}C NMR spectra were obtained on solution in DMSO-d_6 acetone-d_6 and/or $CDCl_3$ as solvent using TMS as internal standard. The data are reported as (*s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet or unresolved, *bs* = broad singlet, coupling constant(s) in Hz, integration). Cyanogen bromide was synthesized based on reported references.[25] Aromatic aldehydes, triethylamine and solvents purchased from Merck and Aldrich without further purification.

General Procedures for the Preparation of 3-arylcyclopropane-1,1,2,2-tetracarbonitriles

In a 10 mL with Teflon-faced screw cap tube equipped by a magnetically stirrer, dissolved 0.106 g (1 mmol) benzaldehyde, 0.132 g (2 mmol) malononitrile, 0.202 g (2 mmol) triethylamine in 5 mL ethanol and then 0.106 g (1 mmol) cyanogen bromide was added into solution at range of 0 °C to room temperature. Cream color solid precipitate immediately during 5 seconds, after about 2 minutes filtered off, washed with ethanol (3 × 3 mL) and dried. (0.218 g, 100% yield).

Triethylammonium dicyanomethanide 4

White crystalline solid; FT-IR (KBr) 3446, 2943, 2738, 2677, 2491, 2166, 1475, 1397, 1036 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.22 (t, 9H, *J* = 6 Hz), 3.00 (m, 6H), 3.77 (s, 1H), 9.03 (bs, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 110.1, 46.7, 9.3, 8.7.

Triethylammonium bromodicyanomethanide 7

White crystalline solid; FT-IR (KBr) 3420, 3047, 2987, 2947, 2804, 2738, 2678, 2491, 2167, 1475, 1035, 565 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.39 (t, 9H, *J* = 7.2 Hz), 3.14 (m, 6H), 9.78 (bs, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.6, 121.6, 46.6, 8.8.

3-Phenylcyclopropane-1,1,2,2-tetracarbonitrile 3a

White crystalline solid, mp 225-227 °C (decompds.) (lit. 229-230 °C[10]); FT-IR (KBr) 3046, 3013, 2928, 2264, 1640, 1374, 1231, 741, 701, 662 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 5.29 (s, 1H), 7.47 (m, 3H), 7.78 (m, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 130.4, 130.0, 129.4, 127.3, 111.4, 109.9, 42.2, 23.6.

3-(2-Nitrophenyl)cyclopropane-1,1,2,2-tetracarbonitrile 3b

White crystalline solid, mp 215-216 °C (decompds.); FT-IR (KBr) 3108, 3089, 3031, 2924, 2866, 2258, 1610, 1530, 1346, 851, 794, 736, 702 cm^{-1}; ^{1}H NMR (Acetone-d_6, 300 MHz) δ 5.45 (s, 1H), 7.96 (t, 1H, *J* = 7.5 Hz), 8.07 (t, 1H, *J* = 7.5 Hz), 8.37 (d, 1H, *J* = 7.5 Hz), 8.51 (d, 1H, *J* = 7.5 Hz); ^{13}C NMR (Acetone-d_6,

75 MHz) δ 147.9, 135.3, 132.7, 132.6, 126.6, 122.0, 110.2, 108.8, 41.7, 23.8.

3-(3-Nitrophenyl)cyclopropane-1,1,2,2-tetracarbonitrile 3c

White crystalline solid, mp 214-216 °C (decompds.); FT-IR (KBr) 3083, 3005, 2258, 2193, 1649, 1528, 1355, 738, 703 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 5.44 (s, 1H), 7.79 (m, 1H), 8.34 (m, 2H), 9.01 (s, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 148.4, 136.9, 131.0, 129.7, 125.6, 125.3, 111.3, 109.9, 46.2, 24.1.

3-(4-Bromophenyl)cyclopropane-1,1,2,2-tetracarbonitrile 3d

White crystalline solid, mp 218-219 °C (decompds.); FT-IR (KBr) 3087, 3061, 3004, 2264, 1622, 1590, 1492, 1401, 1072, 1014, 844, 785, 732, 491 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 5.11 (s, 1H), 7.79 (d, 2H, J = 8.4 Hz), 7.89 (d, 2H, J = 8.4 Hz); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 132.4, 132.3, 126.9, 124.2, 111.4, 109.9, 41.5, 23.7.

3-(4-Chlorophenyl)cyclopropane-1,1,2,2-tetracarbonitrile 3e

White crystalline solid, mp 240-243 °C (decompds.) (lit. 250-251 °C[10]); FT-IR (KBr) 3091, 3066, 2264, 2211, 1624, 1596, 1497, 1404, 1091, 1018, 845, 790, 728, 501 cm^{-1}; ^1H NMR (Acetone-d_6, 300 MHz) δ 5.03 (s, 1H), 7.63 (d, 2H, J = 8.4 Hz), 7.95 (d, 2H, J = 8.4 Hz); ^{13}C NMR (Acetone-d_6, 75 MHz) δ 136.1, 131.4, 129.4, 125.5, 110.4, 108.9, 41.9, 22.9.

3-(3,4,5-Trimethoxyphenyl)cyclopropane-1,1,2,2-tetracarbonitrile 3f

White crystalline solid, mp 227-229 °C (decompds.); FT-IR (KBr) 3047, 2997, 2943, 2842, 2260, 1592, 1512, 1468, 1421, 1251, 1127, 993 cm^{-1}; ^1H NMR (Acetone-d_6, 300 MHz) δ 3.77 (s, 3H), 3.87 (s, 6H), 4.96 (s, 1H), 7.31 (s, 2H); ^{13}C NMR (Acetone-d_6, 75 MHz) δ 153.9, 139.8, 121.4, 110.7, 109.1, 107.2, 59.8, 55.9, 42.9, 22.9.

3-(4-Methoxyphenyl)cyclopropane-1,1,2,2-tetracarbonitrile 3h

White crystalline solid, mp 209-211 °C (decompds.) (lit. 208-210 °C[10]); FT-IR (KBr) 3004, 2968, 2946, 2846, 2264, 1611, 1513, 1468, 1307, 1264, 1183, 1035, 844, 803 cm^{-1}; ^1H NMR (Acetone-d_6, 300 MHz) δ 3.87 (s, 3H), 4.88 (s, 1H), 7.11 (d, 2H, J = 8.7 Hz), 7.80 (d, 2H, J = 8.7 Hz); ^{13}C NMR (Acetone-d_6, 75 MHz) δ 161.3, 131.0, 118.0, 114.6, 110.7, 109.0, 54.9, 42.5, 22.8.

3-(4-Cyanophenyl)cyclopropane-1,1,2,2-tetracarbonitrile 3i

White crystalline solid, mp 225-226 °C (decompds.); FT-IR (KBr) 3102, 3056, 3006, 2365, 2239, 1612, 1513, 1412, 856, 800, 556 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 5.45 (s, 1H), 8.00 (d, 2H, J = 8.4 Hz), 8.11 (d, 2H, J = 8.4 Hz); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 133.2, 132.7, 131.3, 118.5, 113.3, 111.3, 109.8, 41.4, 23.8.

3-(Pyridin-2-yl)cyclopropane-1,1,2,2-tetracarbonitrile 3l

White crystalline solid, mp 173-175 °C (decompds.); FT-IR (KBr) 3049, 2925, 2854, 2260, 2208, 1627, 1591, 1473, 1446, 999, 791, 748, 621 cm^{-1}; ^1H NMR (Acetone-d_6, 300 MHz) δ 4.95 (s, 1H), 7.57 (m, 1H), 7.97-8.02 (m, 2H), 8.68 (m, 1H); ^{13}C NMR (Acetone-d_6, 75 MHz) δ 149.0, 146.2, 137.5, 126.6, 125.2, 111.0, 108.3, 41.7, 21.9.

2-(Anthracen-9-ylmethylene)malononitrile 8m

Orange crystalline solid, mp 207-209 °C (decompds.); FT-IR (KBr) 3056, 3018, 2925, 2857, 2228, 1651, 1621, 1573, 1558, 1321, 1257, 736 cm^{-1}; ^1H NMR (Acetone-d_6, 300 MHz) δ 7.64 (t, 2H, J = 7.8 Hz), 7.72 (t, 2H, J = 8.1 Hz), 8.21-8.24 (m, 4H), 8.85 (s, 1H), 9.48 (s, 1H); ^{13}C NMR (Acetone-d_6, 75 MHz) δ 161.8, 131.5, 131.1, 129.2, 129.1, 128.9, 127.8, 126.0, 124.7, 47.0.

3-(2-formylphenyl)cyclopropane-1,1,2,2-tetracarbonitrile 18a″

White crystalline solid, mp 287-289 °C (decompds.); FT-IR (KBr) 3082, 3063, 3010, 2925, 2869, 2772, 2259, 1682, 1597, 1573, 1204, 760, 729, 676 cm^{-1}; ^1H NMR (Acetone-d_6, 300 MHz) δ 5.08 (s, 1H), 7.94-7.96 (m, 2H), 8.20 (m, 1H), 8.30 (m, 1H), 10.27 (s, 1H); ^{13}C NMR (Acetone-d_6, 75 MHz) δ 193.8, 143.9, 137.2, 134.6, 131.5, 131.4, 119.0, 110.7, 109.2, 41.7, 24.0.

3,3′-(1,3-phenylene)bis(cyclopropane-1,1,2,2-tetracarbonitrile) 19b″

White crystalline solid, mp 255-257 °C (decompds.); FT-IR (KBr) 3009, 2925, 2262, 1613, 1493, 1436, 1360, 1142, 1046, 782 cm^{-1}; ^1H NMR (Acetone-d_6, 300 MHz) δ 5.24 (s, 2H), 7.81 (t, 1H, J = 8.1 Hz), 8.14 (d, 2H, J = 7.8 Hz), 8.44 (s, 1H); ^{13}C NMR (Acetone-d_6, 75 MHz) δ 131.5, 131.2, 130.3, 128.1, 110.4, 108.8, 42.0, 22.8.

ACKNOWLEDGEMENTS

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