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ORIGINAL PAPER

Unclassical Hydrogen Bonds of C–H···N and C–H···Cl in the Crystal Structures of 2-((*E*)-1,3-diarylallylidene) malononitriles

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Abstract The 2-((*E*)-3-(2-nitrophenyl)-1-(4-methoxyphenyl) allylidene)malononitrile and 2-((*E*)-3-(2-chlorophenyl)-1-(4-bromophenyl)allylidene)malononitrile were synthesized and characterized by IR, ^{1}H NMR, and elemental analysis. The molecular structures were further confirmed by X-ray diffraction analysis. The former **1**, $C_{19}H_{13}N_3O_3$, is triclinic, space group P−1, $a = 7.3834(13)$, $b = 10.901(3)$, $c = 11.227(2)$ Å, $\alpha = 88.64(2)$, $\beta = 71.596(14)$, $\gamma = 78.186(18)$, $Z = 2$, $V = 838.5(3)$ Å^3. The unclassical hydrogen bond of C–H···N links the molecules forming polymers. The latter **2**, $C_{36}H_{20}Br_2Cl_2N_4$, is orthorhombic, space group Pnma, $a = 20.900$ (4), $b = 7.0710$ (11), $c = 10.9170$ (18) Å, $Z = 2$, $V = 1613.4(5)$ Å^3. The same hydrogen bond of C–H···N and another type of C–H···Cl hydrogen bond link the adjacent molecules forming polymers along *a* axis.

Keywords Hydrogen bond · Allylidenemalononitrile · Infrared · NMR

Introduction

The ability of carbon atoms to act as proton donors in hydrogen bonds has been recognized in recent years [1, 2], Harmon et al. [3] and Kobayashi et al. [4] studied the C–H···X hydrogen bonds by spectroscope. A survey of crystal structures containing short C–H···O was firstly conducted by Sutor in 1963 [5]. In the recent years, more and more C–H···X hydrogen bonds [6–12] (especially C–H···O) have been postulated in the crystal structure, sometimes they are generally considered as un-classical or non-classical hydrogen bonds [13–15] in the literature. However, the symbol X in C–H···X hydrogen bonds is usually limited to be O [6–12], N [16, 17], or F [18–20], and seldom to be Cl [21, 22] or I [23]. It was well known that as potential hydrogen bond acceptors, 2-((*E*)-3-(2-nitrophenyl)-1-(4-methoxyphenyl)allylidene)malononitrile **1** contains the cyano group, methoxy group and the benzene ring moiety, while **2** contains cyano group, the benzene ring moiety and halogen. However, as hydrogen bond donors, they carry no O–H group or N–H group. This raises an interesting question: do what kinds of forces make the molecules together in the crystals if no classical hydrogen bonds? In this paper, we present the crystal structures of 2-((*E*)-3-(2-nitrophenyl)-1-(4-methoxyphenyl)allylidene)malononitrile **1** and 2-((*E*)-3-(2-chlorophenyl)-1-(4-bromophenyl) allylidene)malononitrile **2**, which were prepared by the reaction of aromatic aldehydes and 1-arylethylidene malononitriles in ionic liquid catalyzed by 10 mol% malononitrile. It is found that the unclassical hydrogen bonds of C–H···N in **1**, C–H···N and C–H···Cl in **2** link the molecules forming polymers.

Experimental

Synthesis of 2-((*E*)-3-(2-nitrophenyl)-1-(4-methoxy phenyl)allylidene)malononitrile 1 and 2-((*E*)-3-(2-chlorophenyl)-1-(4-bromophenyl)allylidene)malononitrile 2

A dry 50 mL flask was charged with aromatic aldehyde (2.0 mmol), malononitrile (0.013 g, 0.2 mmol), 1-arylethy

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lidenemalononitrile (2.0 mmol), and ionic liquid of [bmim$^+$][BF$_4$$^-$] (1 mL). The reaction mixture was stirred at 90 °C for 3–8 h, and then 5 mL water was added to the mixture, the solid was isolated by filtration to remove the ionic liquid. The crude yellow products were washed with water and purified by recrystallization from a mixture of DMF and water to give **1** or **2**. **1**: Pale yellow crystals, 96%, mp 182–184 °C. IR (KBr): 3061, 2221, 1602, 1561, 1532, 1485, 1469, 1444, 1391, 1338, 1323, 1286, 1098, 1071, 1039, 1011, 966, 824, 766, 750. ^{1}H NMR (DMSO-d_6) δ: 7.16 (d, $J = 15.6$ Hz, 1H, CH=), 7.47 ~ 7.55 (m, 5H, ArH), 7.58 (d, $J = 15.6$ Hz, 1H, CH=), 7.85 (d, $J = 8.4$ Hz, 2H, ArH), 8.01 ~ 8.03 (m, 1H, ArH). Anal. Calcd for $C_{18}H_{10}BrClN_2$: C 58.49, H 2.73, N 7.58; found C 58.62, H 2.70, N 7.54. **2**: Pale yellow crystals, 95%, mp 188–190 °C. ^{1}H NMR (DMSO-d_6, δ, ppm): 3.87 (s, 3H, CH_3O), 7.16 (d, $J = 8.4$ Hz, 2H, ArH), 7.36 (d, $J = 15.6$ Hz, 1H, CH), 7.42 (d, $J = 15.6$ Hz, 1H, CH), 7.57 (d, $J = 8.4$ Hz, 2H, ArH), 7.70 ~ 7.71 (m, 1H, ArH), 7.85 ~ 7.89 (m, 1H, ArH), 7.98 (d, $J = 8.0$ Hz, 1H, ArH), 8.10 (d, $J = 8.0$ Hz, 1H, ArH); IR (KBr, v, cm^{-1}): 3084, 3004, 2972, 2839, 2223, 1602, 1569, 1518, 1439, 1420, 1345, 1292, 1254, 1210, 1177, 1103, 1025, 983, 857, 838, 794, 749, 704. Anal. Calcd for $C_{19}H_{13}N_3O_3$: C 68.88, H 3.95, N 12.68; found C 69.01, H 3.87, N 12.57.

X-ray Analysis

A summary of the crystallographic data was given in Table 1. The structure was solved by direct method using SHELXTL [24] program and expanded using Fourier technique. The non-hydrogen atoms were refined anisotropically, the hydrogen atoms were positioned geometrically and refined as riding [C–H = 0.93–0.96 Å and $U_{\text{iso}}(\text{H}) = 1.2\, U_{\text{eq}}(\text{C})$]. A full-matrix least-squares refinement gave final $R = 0.0500$ and $\omega R = 0.1284$ ($R = 0.0494$ and $\omega R = 0.1146$ for **2**) with $\omega = 1/[\sigma^2(F_o^2) + (0.0793P)^2]$ ($\omega = 1/[\sigma^2(F_o^2) + (0.0514\text{P})^2 + 2.4803P]$for**2**),where$P = (F_o^2 + 2F_c^2)/3$.

Analysis

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a TENSOR 27 spectrometer in KBr pellet. ^{1}H NMR spectra were obtained

Table 1 Crystallographic data for **1** and **2**

Compounds	1	2
Empirical formula	$C_{19}\,H_{13}\,N_3\,O_3$	$C_{36}\,H_{20}\,Br_2\,Cl_2\,N_4$
CCDC deposit no.	672173	672174
Color/shape	Pale yellow/Block	Pale yellow/Block
Formula weight	331.32	739.28
Temperature	298(2) K	294(2) K
Crystal system	Triclinic	Orthorhombic
Space group	P−1	Pnma
Unit cell dimensions	$a = 7.3834(13)$ Å, $\alpha = 88.64(2)°$	$a = 20.900(4)$ Å, $\alpha = 90°$
	$b = 10.901(3)$ Å, $\beta = 71.596(14)°$	$b = 7.0710(11)$ Å, $\beta = 90°$
	$c = 11.227(2)$ Å, $\gamma = 78.186(18)°$	$c = 10.9170(18)$ Å, $\gamma = 90°$
Volume	838.5(3) Å^3	1613.4(5) Å^3
Z	2	2
Density (calculated), Mg/m^3	1.312	1.522
Absorption coefficient, mm^{-1}	0.091	2.710
Diffractometer/scan	Rigaku Mercury/ω	CCD area detector/π and ω
F(000)	344	736
Crystal size	0.80 × 0.70 × 0.30 mm	0.28 × 0.26 × 0.12 mm
Theta range for data collection	3.18–25.35°	2.10–26.36°
Limiting indices	$-8 \le h \le 8, -13 \le k \le 13, -11 \le l \le 13$	$-26 \le h \le 23, -6 \le k \le 8, -13 \le l \le 12$
Reflections collected	8120	8904
Independent reflections	3047 [R(int) = 0.0384]	1782 [R(int) = 0.00455]
Data/restraints/parameters	3047/0/228	1782/2/145
Goodness-of-fit on F^2	1.005	1.010
Final R indices [$I > 2\,\sigma\,(I)$]	$R_1 = 0.0500$, $wR_2 = 0.1284$	$R_1 = 0.0494$, $wR_2 = 0.1146$
R indices (all data)	$R_1 = 0.0714$, $wR_2 = 0.1434$	$R_1 = 0.0945$, $wR_2 = 0.1402$
Largest diff. peak and hole	0.297 and −0.235 e A^{-3}	0.969 and −0.906 e A^{-3}

from solution in DMSO-d_6 with Me_4Si as internal standard using an Inova-400 spectrometer. Elemental analyses were carried out using Perkin-Elmer 2400 II analyzer.

Results and Discussion

In the infrared spectrography of **1**, it was observed a sharp band at 2221 cm^{-1} (2223 cm^{-1} for **2**) for the cyano group. The ^1H NMR spectrum of **1** exhibited a doublet identified as hydrogen on the double bond at 7.16 ppm ($J = 15.6$ Hz, 7.36 ppm ($J = 15.6$ Hz) for **2**). Another coupling proton was observed at 7.58 ppm with the same coupling constant ($J = 15.6$ Hz, 7.42 ($J = 15.6$ Hz) for **2**). Obviously, the bigger coupling constant (15.6 Hz) also indicated that compounds **1** and **2** were all trans-alkenes.

The selected bond lengths and bond angles of **1** and **2** are given in Table 2. The structures of **1** and **2**, packing

Table 2 Selected bond lengths (Å) and selected bond angles (°) for **1** and **2**

Selected bond lengths for **2**				Selected bond lengths for **1**			
Br(1)–C(16)	1.896(6)	C(10)–C(11)	1.433(9)	O(1)–C(10)	1.368(2)	C(4)–C(14)	1.462(2)
Cl(1)–C(1)	1.740(6)	C(10)–C(12)	1.443(8)	O(1)–C(13)	1.415(3)	C(7)–C(8)	1.379(2)
N(1)–C(11)	1.133(8)	C(13)–C(14)#1	1.312(10)	O(2)–N(3)	1.214(2)	C(7)–C(12)	1.401(2)
N(2)–C(12)	1.128(8)	C(13)–C(14)	1.312(10)	O(3)–N(3)	1.216(3)	C(8)–C(9)	1.385(2)
C(1)–C(2)	1.378(8)	C(13)–C(14′)#1	1.429(11)	N(1)–C(5)	1.145(2)	C(9)–C(10)	1.381(2)
C(1)–C(6)	1.390(7)	C(13)–C(14′)	1.429(11)	N(2)–C(6)	1.136(2)	C(10)–C(11)	1.385(3)
C(2)–C(3)	1.366(8)	C(14)–C(15)	1.387(13)	N(3)–C(15)	1.469(3)	C(11)–C(12)	1.371(2)
C(3)–C(4)	1.385(9)	C(14)–C(14)#1	2.01(2)	C(1)–C(2)	1.363(2)	C(14)–C(19)	1.394(2)
C(4)–C(5)	1.373(8)	C(15)–C(16)	1.298(12)	C(1)–C(5)	1.431(3)	C(14)–C(15)	1.399(2)
C(5)–C(6)	1.389(8)	C(15)–C(15)#1	2.02(2)	C(1)–C(6)	1.436(2)	C(15)–C(16)	1.375(3)
C(6)–C(7)	1.454(7)	C(14′)–C(15′)	1.386(13)	C(2)–C(3)	1.450(2)	C(16)–C(17)	1.381(3)
C(7)–C(8)	1.327(7)	C(15′)–C(16)	1.413(12)	C(2)–C(7)	1.482(2)	C(17)–C(18)	1.362(3)
C(8)–C(9)	1.422(7)	C(16)–C(15)#1	1.298(12)	C(3)–C(4)	1.328(2)	C(18)–C(19)	1.374(3)
C(9)–C(10)	1.355(8)	C(16)–C(15′)#1	1.413(12)				
C(9)–C(13)	1.491(8)	#1: x, −y + 1/2, z					
Selected bond angles for 2				**Selected bond angles for 1**			
C(2)–C(1)–C(6)	122.7(6)	C(14)–C(13)–C(14′)#1	118.3(6)	C(10)–O(1)–C(13)	117.92(15)	C(7)–C(8)–C(9)	121.57(16)
C(2)–C(1)–Cl(1)	117.3(4)	C(14)#1–C(13)–C(14′)	118.3(6)	O(2)–N(3)–O(3)	122.2(2)	C(10)–C(9)–C(8)	119.10(16)
C(6)–C(1)–Cl(1)	120.0(4)	C(14′)#1–C(13)–C(14′)	108.9(8)	O(2)–N(3)–C(15)	119.42(19)	O(1)–C(10)–C(9)	124.29(16)
C(3)–C(2)–C(1)	119.7(6)	C(14)#1–C(13)–C(9)	123.0(5)	O(3)–N(3)–C(15)	118.3(2)	O(1)–C(10)–C(11)	115.52(15)
C(2)–C(3)–C(4)	119.4(6)	C(14)–C(13)–C(9)	123.0(5)	C(2)–C(1)–C(5)	122.86(15)	C(9)–C(10)–C(11)	120.19(16)
C(5)–C(4)–C(3)	120.2(6)	C(14′)#1–C(13)–C(9)	118.7(5)	C(2)–C(1)–C(6)	121.89(15)	C(12)–C(11)–C(10)	120.27(16)
C(4)–C(5)–C(6)	121.9(6)	C(14′)–C(13)–C(9)	118.7(5)	C(5)–C(1)–C(6)	115.25(15)	C(11)–C(12)–C(7)	120.45(16)
C(1)–C(6)–C(5)	116.1(5)	C(13)–C(14)–C(15)	122.5(10)	C(1)–C(2)–C(3)	119.39(15)	C(19)–C(14)–C(15)	115.21(16)
C(1)–C(6)–C(7)	121.6(5)	C(13)–C(14)–C(14)#1	40.1(4)	C(1)–C(2)–C(7)	120.25(15)	C(19)–C(14)–C(4)	120.52(16)
C(5)–C(6)–C(7)	122.2(5)	C(15)–C(14)–C(14)#1	90.2(6)	C(3)–C(2)–C(7)	120.36(15)	C(15)–C(14)–C(4)	124.20(16)
C(8)–C(7)–C(6)	126.8(5)	C(16)–C(15)–C(14)	120.8(10)	C(4)–C(3)–C(2)	124.55(16)	C(16)–C(15)–C(14)	122.71(18)
C(7)–C(8)–C(9)	125.1(5)	C(16)–C(15)–C(15)#1	39.1(5)	C(3)–C(4)–C(14)	124.16(15)	C(16)–C(15)–N(3)	116.70(18)
C(10)–C(9)–C(8)	120.5(5)	C(14)–C(15)–C(15)#1	89.8(6)	N(1)–C(5)–C(1)	178.35(19)	C(14)–C(15)–N(3)	120.57(17)
C(10)–C(9)–C(13)	119.1(5)	C(15′)–C(14′)–C(13)	119.2(9)	C(8)–C(7)–C(12)	118.35(15)	C(15)–C(16)–C(17)	119.4(2)
C(8)–C(9)–C(13)	120.4(5)	C(14′)–C(15′)–C(16)	118.4(9)	C(8)–C(7)–C(2)	120.83(15)	C(18)–C(17)–C(16)	120.00(19)
C(9)–C(10)–C(11)	121.8(5)	C(15)#1–C(16)–C(15)	101.9(9)	C(12)–C(7)–C(2)	120.79(15)	C(17)–C(18)–C(19)	119.92(19)
C(9)–C(10)–C(12)	123.8(5)	C(15)#1–C(16)–C(15′)	120.7(7)	C(18)–C(19)–C(14)	122.79(18)		
C(11)–C(10)–C(12)	114.4(5)	C(15)–C(16)–C(15′)#1	120.7(7)				
N(1)–C(11)–C(10)	179.1(6)	C(15′)–C(16)–C(15′)#1	110.6(8)				
N(2)–C(12)–C(10)	177.7(7)	C(15)#1–C(16)–Br(1)	120.9(5)				
C(15′)#1–C(16)–Br(1)	118.3(5)	C(15)–C(16)–Br(1)	120.9(5)				
C(15′)–C(16)–Br(1)	118.3(5)	#1: x, −y + 1/2, z					

Table 3 Unclassical hydrogen bonds geometry for **1** and **2**

(*D*–H···*A*)	*D*–H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*–H···*A*(°)	Symmetry codes
C(18)–H(18)···N(1)	0.93	2.61	3.348(3)	137.2	$x-1, y+1, z$
C(15)–H(15A)···Cl(1)	0.93	2.90	3.793(2)	161.0	$1-x, -y, 1-z$
C(14)–H(14A)···N(2)	0.93	2.56	3.313(2)	138.8	$1-x, -0.5+y, -z$

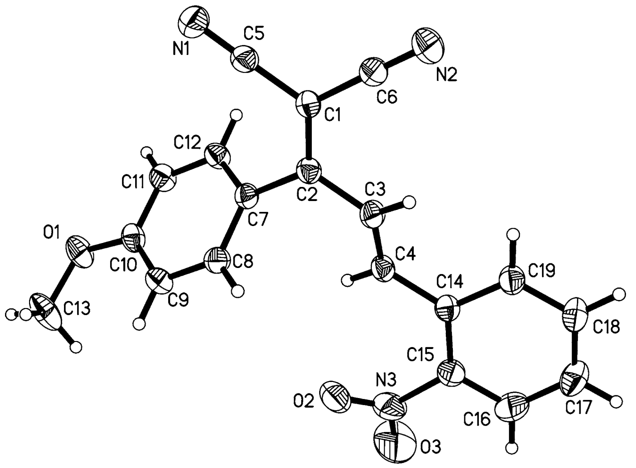

Fig. 1 The molecular structure of **1** showing 50% probability displacement ellipsoids

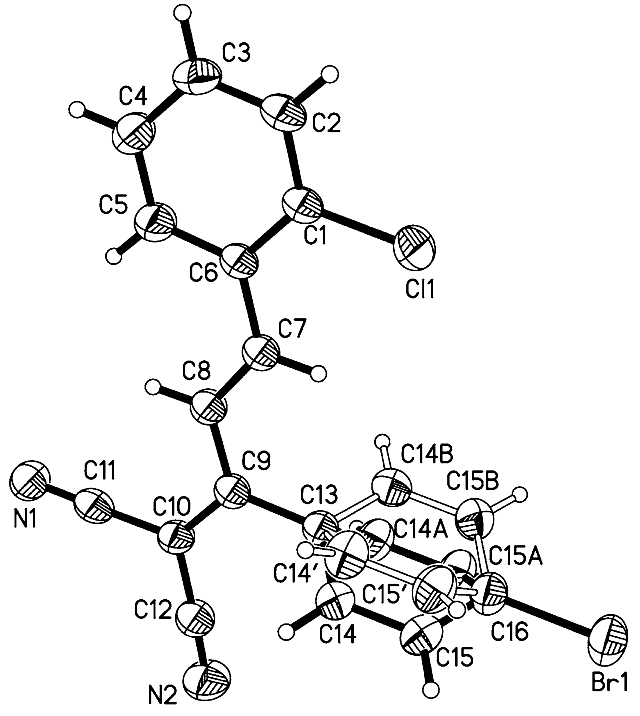

Fig. 2 The molecular structure of **2** showing 50% probability displacement ellipsoids

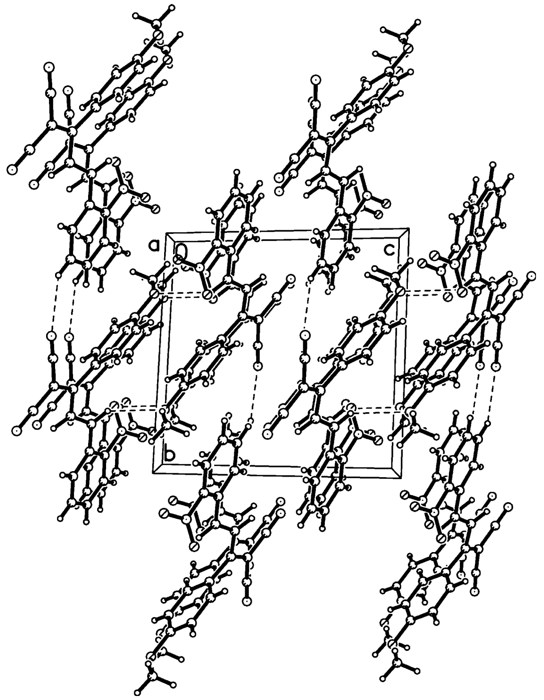

Fig. 3 The packing arrangement in a unit cell of **1** along *a*

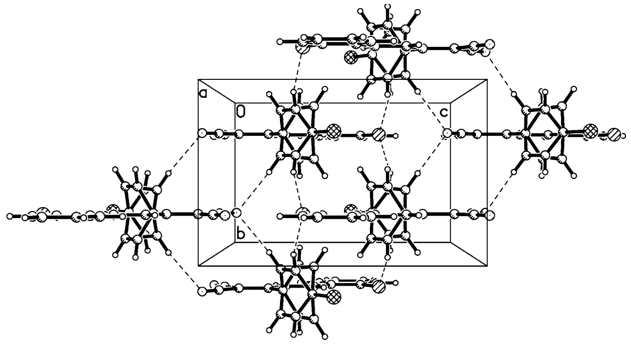

Fig. 4 The packing arrangement in a unit cell of **2** along *a*

arrangement in a unit cell of **1** and **2** are shown in Figs. 1, 2, 3, and 4 respectively. In **1**, the atoms C(14)/C(4)/H(14)/C(3)/H(3)/C(2) are coplanar, and two larger groups containing benzene rings are the other side of double bonds, forming trans-conformation. The basal plane of the alkene makes dihedral rings to benzene rings C(14)–C(19) and C(7)–C(12) of 22.9(1)° and 62.4(1)°, respectively. The benzene rings make a dihedral angle of 52.7(1)° with one another. In **2**, the alkene also forms trans-conformation. However, the benzene ring and the atoms C(6)–C(9)/H(7)/H(8) are coplanar, which makes a dihedral angle of 67.0(1)° with benzene ring C(13)–C(16)/C(14B)/C(15B).

The X-ray determination indicates that two types of unclassical hydrogen bonds C–H···Cl and C–H···N are presented in **2**. From Table 3, it is clear to find that the distance from H(15A) to Cl(1) in the adjacent molecules is 2.90 Å, which is obviously shorter than the sum of the van der Waals radii for Cl and H (3.00 Å), indicating the presence of unclassical hydrogen bonds C–H···Cl. On the other hand, there is another different type of intermolecular hydrogen bonds in the vicinal molecules to be found: C(14)–H(14A)···N(2) according to the distance measurement (2.56 Å for H(14A)···N(2)) and the related bond angles (138.8° for C(14)–H(14A)···N(2)) (Table 3). In **1**, the intermolecular hydrogen bond of C(18)–H(18)···N(1) is observed according to the data listed in Table 3, The unclassical hydrogen bonds of C–H···N in **1** and the C–H···N and C–H···Cl hydrogen bonds in **2** all link the molecules forming polymers, respectively (Figs. 3 and 4).

Supplementary Material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-672173 and CCDC-672174. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0) 1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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