

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

3-(Dicyanomethylidene)-6,6-dimethylcyclohexa-1,4-diene

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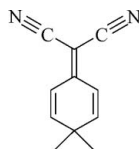
Received 11 October 2007; accepted 15 October 2007

Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.051; wR factor = 0.132; data-to-parameter ratio = 18.4.

In the title compound, $\text{C}_{11}\text{H}_{10}\text{N}_2$, the six-membered ring is planar (r.m.s.d. 0.013 Å). Molecules are linked by weak $\text{C}-\text{H}\cdots\text{N}$ interactions into chains parallel to [201], which lie in planes parallel to $(\bar{1}02)$.

Related literature

For related literature, see: Hopf (1984, 2001); Hopf *et al.* (2002); Yanagita *et al.* (1951).



Experimental

Crystal data

$\text{C}_{11}\text{H}_{10}\text{N}_2$
 $M_r = 170.21$
 Monoclinic, $P2_1/c$
 $a = 7.8978$ (8) Å
 $b = 18.534$ (2) Å
 $c = 6.8486$ (6) Å
 $\beta = 103.232$ (8)°

$V = 975.88$ (17) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.07$ mm⁻¹
 $T = 173$ (2) K
 $0.6 \times 0.6 \times 0.6$ mm

Data collection

Siemens P4 diffractometer
 Absorption correction: none
 3180 measured reflections
 2226 independent reflections
 1716 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.013$
 3 standard reflections
 every 247 reflections
 intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.132$
 $S = 1.05$
 2226 reflections

121 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.50$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.41$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C5}-\text{H5}\cdots\text{N1}^i$	0.95	2.65	3.4007 (17)	136

Symmetry code: (i) $x - 1, -y + \frac{3}{2}, z - \frac{1}{2}$.

Data collection: XSCANS (Fait, 1991); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP5 (Siemens, 1994); software used to prepare material for publication: SHELXL97.

We thank Mr A. Weinkauff for technical assistance.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2538).

References

- Fait, J. (1991). XSCANS. Siemens X-Ray Analytical Instruments Inc., Madison, Wisconsin, USA.
 Hopf, H. (1984). *Angew. Chem. Int. Ed. Engl.* **23**, 948–960.
 Hopf, H. (2001). *Angew. Chem. Int. Ed.* **40**, 705–707.
 Hopf, H., Kämpen, J., Bubenitschek, P. & Jones, P. G. (2002). *Eur. J. Org. Chem.* pp. 1708–1721.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1997). SHELXL97. University of Göttingen, Germany.
 Siemens (1994). XP. Version 5.03. Siemens Analytical X-Ray Instruments, Madison, Wisconsin, USA.
 Yanagita, M., Tahara, A. & Ohki, E. (1951). *J. Pharm. Soc. Jpn.* **71**, 1060–1064.

supplementary materials

Acta Cryst. (2007). E63, o4351 [doi:10.1107/S160053680705060X]

3-(Dicyanomethylidene)-6,6-dimethylcyclohexa-1,4-diene

J. Kämpen, P. G. Jones, P. Bubenitschek and H. Hopf

Comment

In our studies of the preparation and properties of novel cross-conjugated π -electron systems (Hopf, 1984, 2001; Hopf *et al.*, 2002), we needed the structure of the title compound **3** for comparison; see Fig. 1.

The molecular dimensions (Table 1) accord with expectation. The six-membered ring is planar (r.m.s. deviation 0.013 Å), with the dicyanomethylidene group bent out of the plane by up to 0.179 (3) Å for N2.

The packing involves chains of molecules parallel to (201), linked *via* the weak hydrogen bond H5 \cdots N1 (Table 2). This interaction might be better considered as an H $\cdots\pi$ interaction to the midpoint of C8 \equiv N1, which is slightly more linear (H \cdots midpoint 2.76 Å, angle 148°). The chains lie in planes parallel to $\bar{1}02$ (Fig. 2).

Experimental

The preparation of (**3**) was achieved by Knoevenagel condensation of 4,4-dimethylcyclohexa-2,5-dione (**1**) (Yaganita *et al.*, 1951) with malonodinitrile (**2**). 10 mg β -alanine and 0.2 ml glacial acetic acid were added to a mixture of 0.49 g (4.0 mmol) **1** and 0.26 g (4.0 mmol) of freshly distilled **2** in 8 ml anhydrous ethanol. After stirring for several days (TLC monitoring), 40 ml dichloromethane were added and the reaction mixture filtered through a short silica gel column. The solvent was removed by rotary evaporation and the remaining solid purified by plate chromatography (silica gel, dichloromethane): 0.20 g (30%) **3**, colourless needles, m.p. 94°C. Single crystals were obtained from dichloromethane.

$^1\text{H-NMR}$: δ = 1.25 (s, 6H, CH₃), 6.67 (d, J = 9.9 Hz, 2H, 1- and 5-H), 6.82 (d, J = 9.9 Hz, 2- and 4-H); $^{13}\text{C-NMR}$: δ = 26.6 (CH₃), 39.8 (C6), 76.5 (C7), 112.9 (C \equiv N), 120.5 (C2,C4), 154.5 (C1,C5), 157.0 (C3); IR (KBr): $\bar{\nu}$ = 1972 (*m*), 2935 (*m*), 2219 (*s*), 1650 (*s*), 1641 (*s*), 1525 (*s*), 1474 (*m*), 924 (*w*), 825 (*s*), 690 (*w*) cm^{-1} ; UV (acetonitrile): λ_{max} (log ϵ) = 322 nm (4.40); MS (EI, 70 eV): m/z = 170 (31) [M^+], 156 (11), 155 (100), 143 (15), 128 (35), 115 (12), 105 (23), 101 (19), 91 (14); elemental analysis: C₁₁H₁₀N₂ (170.23): calcd C 77.62, H 5.92, N 16.46; found C 77.31, H 5.94, N 16.40.

Refinement

Methyl H atoms were identified in difference syntheses, idealized and then refined using rigid methyl groups (C—H 0.98 Å, H—C—H 109.5°) allowed to rotate but not tip. Other H atoms were included using a riding model with C—H 0.95 Å. U(H) values were fixed at $n \times U(\text{eq})$ of the parent atom, with $n = 1.5$ for methyl H, 1.2 for other H.

Figures

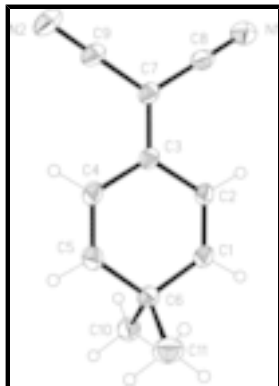


Fig. 1. The molecule of the title compound in the crystal. Ellipsoids represent 30% probability levels.

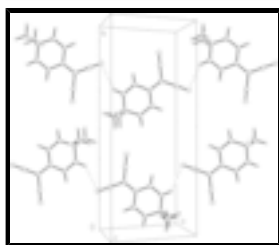


Fig. 2. Packing diagram of the title compound viewed perpendicular to the plane $\bar{1}02$.



3-(Dicyanomethylidene)-6,6-dimethylcyclohexa-1,4-diene

Crystal data

$C_{11}H_{10}N_2$

$M_r = 170.21$

Monoclinic, $P2_1/c$

$a = 7.8978$ (8) Å

$b = 18.534$ (2) Å

$c = 6.8486$ (6) Å

$\beta = 103.232$ (8)°

$V = 975.88$ (17) Å³

$Z = 4$

$F_{000} = 360$

$D_x = 1.159$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 62 reflections

$\theta = 5\text{--}12.5^\circ$

$\mu = 0.07$ mm⁻¹

$T = 173$ (2) K

Block, colourless

$0.6 \times 0.6 \times 0.6$ mm

Data collection

Siemens P4
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 173$ (2) K

ω scans

$R_{int} = 0.013$

$\theta_{max} = 27.5^\circ$

$\theta_{min} = 3.3^\circ$

$h = -10 \rightarrow 9$

$k = -6 \rightarrow 24$

Absorption correction: none $l = 0 \rightarrow 8$
 3180 measured reflections 3 standard reflections
 2226 independent reflections every 247 reflections
 1716 reflections with $I > 2\sigma(I)$ intensity decay: none

Refinement

Refinement on F^2 Hydrogen site location: inferred from neighbouring sites
 Least-squares matrix: full H-atom parameters constrained
 $R[F^2 > 2\sigma(F^2)] = 0.051$ $w = 1/[\sigma^2(F_o^2) + (0.0892P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.132$ $(\Delta/\sigma)_{\max} < 0.001$
 $S = 1.05$ $\Delta\rho_{\max} = 0.50 \text{ e } \text{\AA}^{-3}$
 2226 reflections $\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$
 121 parameters Extinction correction: SHELXL97 (Sheldrick, 1997),
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Primary atom site location: structure-invariant direct methods Extinction coefficient: 0.34 (3)
 Secondary atom site location: difference Fourier map

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Least-squares planes (x, y, z in crystal coordinates) and deviations from them (* indicates atom used to define plane)

$$-4.0384 (0.0036) x + 0.2071 (0.0092) y + 6.5304 (0.0014) z = 0.0741 (0.0061)$$

$$* 0.0103 (0.0009) C1 * 0.0083 (0.0008) C2 * -0.0187 (0.0008) C3 * 0.0093 (0.0009) C4 * 0.0093 (0.0010) C5 * -0.0185 (0.0009) C6 - 0.0826 (0.0017) C7 - 0.1204 (0.0022) C8 - 0.1269 (0.0022) C9 - 0.1396 (0.0028) N1 - 0.1789 (0.0026) N2$$

Rms deviation of fitted atoms = 0.0132

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	1.01120 (16)	0.68467 (7)	0.5936 (2)	0.0572 (4)
N2	0.68155 (18)	0.86921 (6)	0.37784 (19)	0.0547 (4)
C1	0.46171 (16)	0.56316 (6)	0.28058 (18)	0.0369 (3)
H1	0.4818	0.5128	0.2978	0.044*

supplementary materials

C2	0.59169 (15)	0.60762 (6)	0.35924 (17)	0.0343 (3)
H2	0.6999	0.5882	0.4293	0.041*
C3	0.57112 (15)	0.68519 (6)	0.33993 (16)	0.0320 (3)
C4	0.40267 (16)	0.71260 (6)	0.23917 (18)	0.0396 (3)
H4	0.3838	0.7632	0.2287	0.048*
C5	0.27336 (17)	0.66755 (7)	0.1606 (2)	0.0460 (4)
H5	0.1648	0.6881	0.0958	0.055*
C6	0.28664 (15)	0.58718 (7)	0.1671 (2)	0.0418 (3)
C7	0.70796 (15)	0.73089 (6)	0.41331 (16)	0.0338 (3)
C8	0.87590 (16)	0.70475 (7)	0.51221 (18)	0.0398 (3)
C9	0.69184 (17)	0.80778 (7)	0.39413 (18)	0.0391 (3)
C10	0.2557 (2)	0.55870 (7)	-0.0502 (2)	0.0539 (4)
H10A	0.1400	0.5735	-0.1254	0.081*
H10B	0.2634	0.5059	-0.0484	0.081*
H10C	0.3442	0.5786	-0.1146	0.081*
C11	0.14710 (19)	0.55525 (9)	0.2676 (3)	0.0624 (5)
H11A	0.0315	0.5708	0.1938	0.094*
H11B	0.1675	0.5723	0.4065	0.094*
H11C	0.1537	0.5025	0.2663	0.094*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0466 (7)	0.0505 (7)	0.0686 (8)	-0.0086 (5)	0.0015 (6)	0.0017 (6)
N2	0.0815 (9)	0.0309 (6)	0.0557 (7)	-0.0078 (5)	0.0242 (6)	-0.0056 (5)
C1	0.0433 (7)	0.0250 (5)	0.0409 (6)	0.0024 (4)	0.0068 (5)	0.0015 (5)
C2	0.0383 (6)	0.0269 (6)	0.0358 (6)	0.0040 (4)	0.0047 (5)	0.0030 (4)
C3	0.0422 (6)	0.0260 (5)	0.0280 (5)	0.0003 (4)	0.0086 (4)	-0.0009 (4)
C4	0.0472 (7)	0.0241 (5)	0.0447 (6)	0.0064 (5)	0.0045 (5)	-0.0019 (5)
C5	0.0408 (7)	0.0318 (6)	0.0593 (8)	0.0091 (5)	-0.0013 (6)	-0.0033 (6)
C6	0.0389 (7)	0.0291 (6)	0.0531 (7)	0.0001 (5)	0.0018 (5)	-0.0038 (5)
C7	0.0451 (6)	0.0281 (6)	0.0292 (5)	-0.0028 (4)	0.0103 (4)	-0.0011 (4)
C8	0.0436 (7)	0.0352 (6)	0.0399 (6)	-0.0100 (5)	0.0083 (5)	-0.0017 (5)
C9	0.0529 (7)	0.0314 (6)	0.0350 (6)	-0.0066 (5)	0.0146 (5)	-0.0045 (5)
C10	0.0612 (9)	0.0363 (7)	0.0545 (8)	-0.0005 (6)	-0.0070 (7)	-0.0055 (6)
C11	0.0453 (8)	0.0536 (9)	0.0890 (12)	-0.0061 (7)	0.0170 (8)	-0.0039 (8)

Geometric parameters (\AA , $^\circ$)

N1—C8	1.1481 (17)	C5—H5	0.9500
N2—C9	1.1451 (17)	C6—C11	1.544 (2)
C1—C2	1.3303 (17)	C6—C10	1.5451 (19)
C1—C6	1.4905 (17)	C7—C8	1.4288 (18)
C1—H1	0.9500	C7—C9	1.4341 (16)
C2—C3	1.4495 (15)	C10—H10A	0.9800
C2—H2	0.9500	C10—H10B	0.9800
C3—C7	1.3745 (16)	C10—H10C	0.9800
C3—C4	1.4436 (16)	C11—H11A	0.9800
C4—C5	1.3334 (18)	C11—H11B	0.9800

C4—H4	0.9500	C11—H11C	0.9800
C5—C6	1.4933 (17)		
C2—C1—C6	124.33 (10)	C5—C6—C10	108.51 (11)
C2—C1—H1	117.8	C11—C6—C10	109.07 (12)
C6—C1—H1	117.8	C3—C7—C8	122.10 (10)
C1—C2—C3	121.16 (10)	C3—C7—C9	122.20 (11)
C1—C2—H2	119.4	C8—C7—C9	115.70 (10)
C3—C2—H2	119.4	N1—C8—C7	178.94 (14)
C7—C3—C4	121.29 (10)	N2—C9—C7	178.86 (14)
C7—C3—C2	121.03 (10)	C6—C10—H10A	109.5
C4—C3—C2	117.67 (10)	C6—C10—H10B	109.5
C5—C4—C3	120.62 (11)	H10A—C10—H10B	109.5
C5—C4—H4	119.7	C6—C10—H10C	109.5
C3—C4—H4	119.7	H10A—C10—H10C	109.5
C4—C5—C6	124.79 (11)	H10B—C10—H10C	109.5
C4—C5—H5	117.6	C6—C11—H11A	109.5
C6—C5—H5	117.6	C6—C11—H11B	109.5
C1—C6—C5	111.34 (10)	H11A—C11—H11B	109.5
C1—C6—C11	108.95 (12)	C6—C11—H11C	109.5
C5—C6—C11	110.07 (11)	H11A—C11—H11C	109.5
C1—C6—C10	108.86 (11)	H11B—C11—H11C	109.5
C6—C1—C2—C3	0.20 (19)	C2—C1—C6—C10	117.14 (14)
C1—C2—C3—C7	-176.99 (11)	C4—C5—C6—C1	2.35 (19)
C1—C2—C3—C4	2.36 (16)	C4—C5—C6—C11	123.28 (15)
C7—C3—C4—C5	176.90 (12)	C4—C5—C6—C10	-117.44 (15)
C2—C3—C4—C5	-2.44 (17)	C4—C3—C7—C8	-179.56 (11)
C3—C4—C5—C6	0.0 (2)	C2—C3—C7—C8	-0.24 (16)
C2—C1—C6—C5	-2.44 (18)	C4—C3—C7—C9	-0.09 (16)
C2—C1—C6—C11	-124.02 (14)	C2—C3—C7—C9	179.23 (10)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C5—H5 \cdots N1 ⁱ	0.95	2.65	3.4007 (17)	136

Symmetry codes: (i) $x-1, -y+3/2, z-1/2$.

Fig. 1

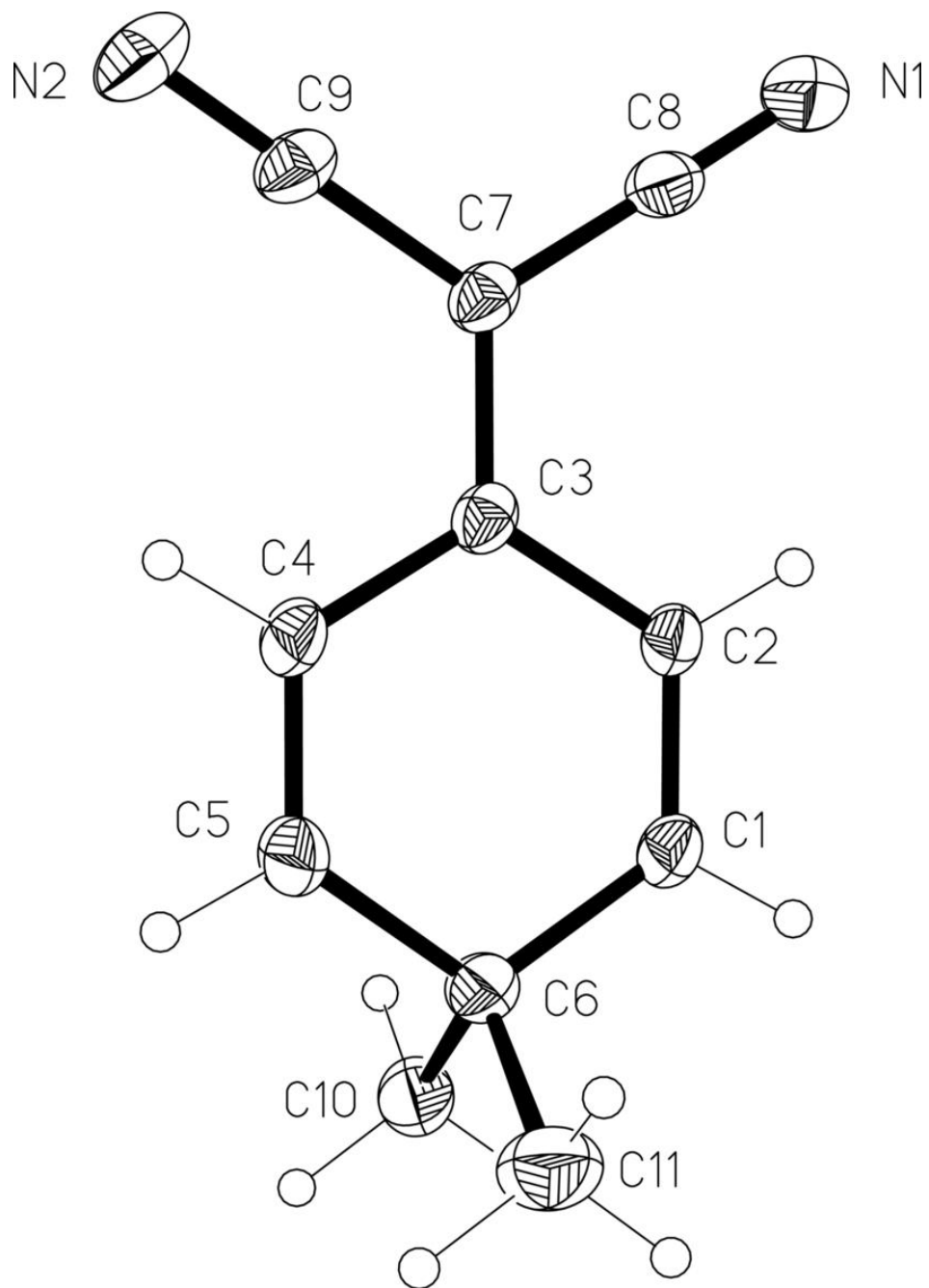


Fig. 2

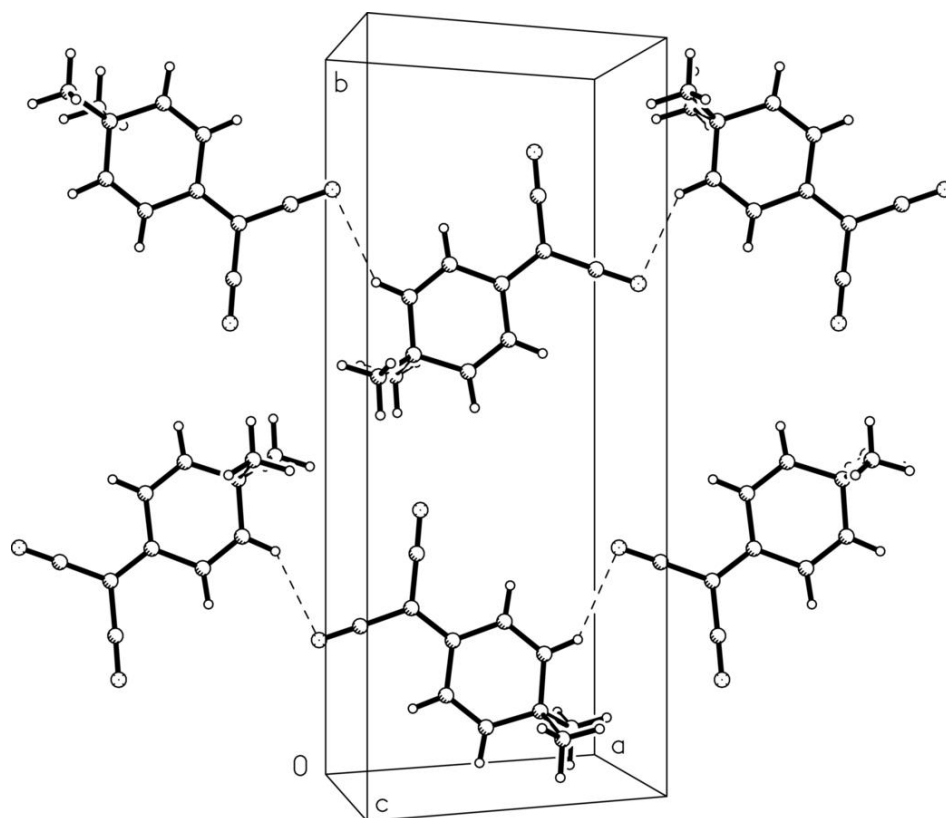


Fig. 3

