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[(2-Methoxyanilino)methylene]malononitrile

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Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.003 Å
R factor = 0.069
wR factor = 0.183
Data-to-parameter ratio = 13.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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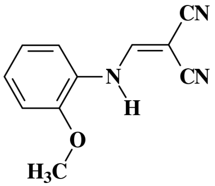
In the structure of the title compound, $C_{11}H_9N_3O$, the molecule is almost planar; the dihedral angle between the *o*-methoxyaniline and dicyanoethylene fragments is 4.8 (1)°. There is a weak conjugation between these fragments of the molecule. An intramolecular N—H···O hydrogen bond forms a planar five-membered ring. Molecules form stacks with head-to-head orientations in the crystal. Weak intermolecular C—H···N hydrogen bonds link molecules into centrosymmetric dimers.

Comment

The present work is part of our project on the synthesis and structural investigation of organic potential non-linear optical compounds. We have investigated a large series of polar molecules that have a dicyano group as an acceptor unit and various donor groups connected by π-conjugated chains of different lengths (Antipin, Clark *et al.*, 1998; Antipin, Timofeeva *et al.*, 1998; Timofeeva, Nesterov, Antipin *et al.*, 2000; Timofeeva, Nesterov, Dolgushin *et al.*, 2000; Nesterov, Antipin *et al.*, 2000; Nesterov, Deng *et al.*, 2000; Nesterov *et al.*, 2002). Continuing our investigations in this direction, we have synthesized and investigated the structure of [(2-methoxyanilino)methylene]malononitrile, (I) (see Fig. 1), which contains an N atom between the donor and acceptor parts of the molecule.



(I)

The X-ray analysis shows that molecule (I) has an almost planar structure in spite of the presence of an intramolecular steric contact H6*A*···H8*A* of 2.18 Å, that is comparable with the sum of the van der Waals radii of these atoms (Rowland & Taylor, 1996). The dihedral angle between the *o*-methoxyaniline and dicyanoethylene fragments is only 4.8 (1)°. On the other hand, the mutual orientation of atom H1*A*, that is bonded to N1, and atom O1 of the methoxy group in the molecule results in an intramolecular hydrogen bond (N1—H1*A*···O1) that creates a five-membered ring and helps to flatten the molecule. Such a planar structure is favorable for conjugation between the donor and acceptor parts of the molecule. According to the values of the bond lengths (Table 1), the trigonal atom N1 has stronger conjugation with double bond C8═C9 than with the aromatic ring. The single

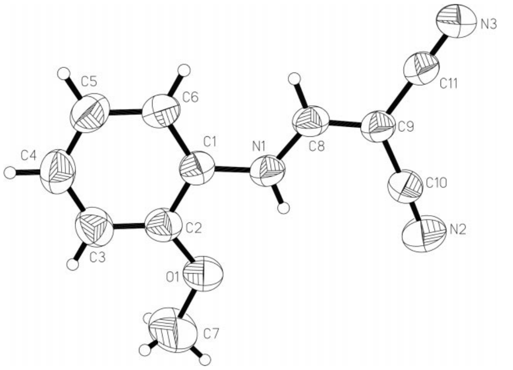


Figure 1
View of the title molecule, (I), with the atom-numbering scheme. The non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as circles of arbitrary radius.

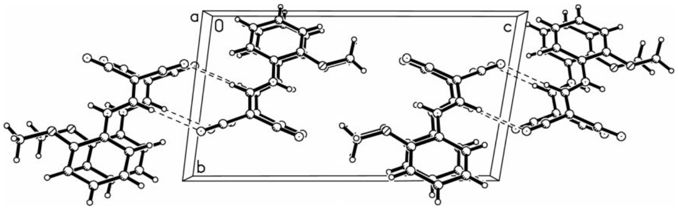


Figure 2
Projection of the crystal packing of compound (I) along the *a* axis. Dashed lines indicate weak C—H···N hydrogen bonds.

C1—N1 bond is only slightly shorter than the standard value for such bonds (Allen *et al.*, 1987). Thus, the presence of N is less favorable for conjugation between the two parts of the molecule.

Molecules in the crystal form stacks with head-to-head orientations (see Fig. 2). Weak intermolecular hydrogen bonds [C8—H8*A*···N3^{i}; symmetry code: (i) $2 - x$, $1 - y$, $-z$] (see Table 2) link the molecules into centrosymmetric dimers. According to our previous data, similar hydrogen bonds were found when molecules crystallized in centrosymmetric space groups (Antipin, Timofeeva *et al.*, 1998; Nesterov, Deng *et al.*, 2000). The other bond distances in the current molecule have standard values (Allen *et al.*, 1987).

Experimental

The title compound, (I), was obtained by the reaction of *o*-methoxyaniline (0.005 mol) with (ethoxymethylene)malononitrile (0.005 mol) in ethanol (20 ml) at room temperature. The precipitate was isolated and recrystallized from ethanol (melting point 491 K, yield 79%). Light yellow crystals were obtained by isothermic evaporation of an ethanolic solution of (I).

Crystal data

$C_{11}H_9N_3O$
$M_r = 199.21$
Triclinic, $P\bar{1}$
$a = 4.5893$ (18) Å
$b = 8.105$ (4) Å
$c = 14.641$ (7) Å
$\alpha = 97.77$ (4)°
$\beta = 91.18$ (4)°
$\gamma = 103.48$ (3)°
$V = 523.9$ (4) Å^3

$Z = 2$
$D_x = 1.263$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 11$–12°
$\mu = 0.09$ mm^{-1}
$T = 297$ (2) K
Prism, light yellow
0.45 × 0.35 × 0.20 mm

Data collection

Siemens *P*3/PC diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2065 measured reflections
1820 independent reflections
1389 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.066$

$\theta_{\max} = 25.1°$
$h = 0 \rightarrow 5$
$k = -9 \rightarrow 9$
$l = -17 \rightarrow 17$
3 standard reflections every 97 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.183$
$S = 1.10$
1820 reflections
137 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1222P)^2 + 0.0112P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C8	1.322 (2)	C8—C9	1.363 (3)
N1—C1	1.412 (3)	C9—C10	1.421 (3)
N2—C10	1.142 (3)	C9—C11	1.427 (3)
N3—C11	1.142 (3)		
C8—N1—C1	126.95 (16)	N2—C10—C9	177.4 (2)
O1—C2—C3	125.71 (18)	N3—C11—C9	178.5 (2)
N1—C8—C9	124.80 (17)		
C8—N1—C1—C2	176.26 (17)	C1—N1—C8—C9	−179.68 (17)
C7—O1—C2—C3	−0.1 (4)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1	0.86	2.18	2.584 (3)	108
C8—H8*A*···N3^{i}	0.93	2.42	3.305 (3)	160

Symmetry code: (i) $2 - x$, $1 - y$, $-z$.

All H atoms were included in calculated positions, with C—H distances of 0.93 Å (0.96 Å for methyl) and 0.86 Å for N—H. They were included in the refinement in riding-motion approximation, with $U_{\rm iso} = 1.2U_{\rm eq}$ ($U_{\rm iso} = 1.5U_{\rm eq}$ for methyl) of the carrier atom.

Data collection: *P*3/*PC* (Siemens, 1989); cell refinement: *P*3/*PC*; data reduction: *SHELXTL* (Sheldrick, 1994); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXL*97.

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