

the two acceptor atoms, O(1)A and O(1)B, at the H atom is 76 (1)° (Jeffrey & Maluszynska, 1981). An N(aryl)—H...O(sulfonyl) contact between a type B aryl amino group and a type A sulfonyl O atom could also be a possible weak hydrogen-bond-like contact if allowance is made for the fact that the H atom appears to have refined to a position too close to the N atom. The geometrical details of the hydrogen bonds and the possible hydrogen-bond-like contacts and their symmetry codes are as follows:

A—H...B	A—H (Å)	A...B (Å)	H...B (Å)	∠A—H...B (°)
N(1)A—H(1)A...N(3)B ⁱ	0.90 (4)	2.900 (4)	2.01 (4)	170 (4)
N(2)A—H(2)A...O(1)A ⁱⁱ	0.83 (6)	3.176 (5)	2.59 (6)	129 (5)
N(2)A—H(2)A...O(1)B ^{ii*}	0.83 (6)	3.477 (8)	2.71 (6)	155 (5)
∠O(1)A ⁱⁱ ...H(2)A...O(1)B ⁱⁱ = 76 (1)°				
N(2)A—H(2)A...O(3)B ⁱⁱⁱ	0.93 (5)	3.180 (6)	2.34 (5)	149 (4)
N(1)B—H(1)B...O(1)A ⁱ	0.73 (4)	2.883 (4)	2.16 (4)	170 (4)
N(2)B—H(2)B...O(2)B ⁱⁱ	0.83 (5)	2.999 (5)	2.17 (5)	171 (4)
N(2)B—H(2)B...O(1)A ^{iv*}	0.64 (5)	3.439 (5)	2.80 (5)	172 (5)

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

* Possible hydrogen-bond-like contacts.

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Structure of a Condensation Product of Isopropylidenemalononitrile under Basic Conditions, 5-Amino-3-methoxy-1,8,8-trimethyl-2-azabicyclo[2.2.2]octa-2,5-diene-4,6-dicarbonitrile

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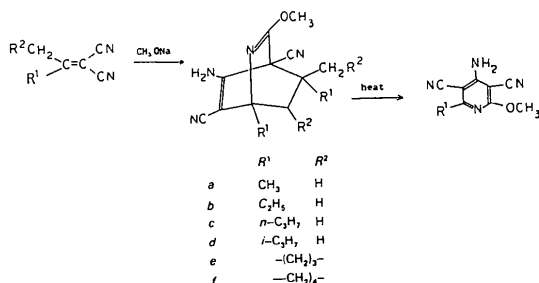
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Abstract. C₁₃H₁₆N₄O, $M_r = 244.3$, triclinic, $P\bar{1}$, $a = 12.541$ (2), $b = 13.404$ (3), $c = 8.733$ (1) Å, $\alpha = 93.93$ (2), $\beta = 90.44$ (3), $\gamma = 63.17$ (2)°, $V = 1306.5$ Å³, $Z = 4$, $D_m = 1.242$, $D_x = 1.241$ g cm⁻³, $\text{Mo K}\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.897$ cm⁻¹, $F(000) = 520$, room temperature, final $R = 0.052$ for 2487 reflections [$|F_o| > 2.5\sigma(|F_o|)$]. A condensation product obtained from isopropylidenemalononitrile was determined to be a 2-azabicyclo[2.2.2]octane derivative. There are two crystallographically independent molecules in the unit cell, which are very similar. The

main ring of the molecule has a bridged dihydropyridine skeleton with a short C=N bond and a long C—C(NH₂) bond. The molecules are held together by hydrogen bonding to form chains along the a axis.

Introduction. Alkylidenemalononitriles undergo anomalous self-condensation in the presence of methoxide ion to give a product as shown below (Igarashi, Nakano, Takezawa, Wantanabe & Sato, 1987); the products (except those obtained from cycloalkylidenemalononitriles) degrade to substituted pyridine

derivatives with loss of hydrocarbon. The compound was found to consist of a methanol molecule and two molecules of starting material. The molecular structure of the product ($R^1 = \text{CH}_3$ and $R^2 = \text{H}$) was determined to be 5-amino-3-methoxy-1,8,8-trimethyl-2-azabicyclo-[2.2.2]octa-2,5-diene-4,6-dicarbonitrile by the X-ray diffraction method.



Experimental. Single crystals obtained from ethanolic solution. D_m measured by flotation in aqueous potassium iodide. Rigaku AFC 3 diffractometer at The Institute for Solid State Physics, graphite-monochromated $\text{MoK}\alpha$; colorless plate crystal, approximately $0.2 \times 0.4 \times 0.1$ mm; lattice parameters determined by least-squares refinement from setting angles of 34 accurately adjusted reflections ($25 < 2\theta < 44^\circ$). Intensities collected by ω - 2θ scan up to $2\theta = 45^\circ$; 3457 independent reflections ($-13 \leq h \leq 13$, $-14 \leq k \leq 0$, $-9 \leq l \leq 9$) measured; 2487 observed with $F_o > 2.5\sigma(F_o)$; four standard reflections measured every 50 reflections: during the measurement no significant deterioration. Lorentz and polarization corrections applied, but no absorption correction. Structure solved by the direct method (*MULTAN78*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Two cyano groups and a methoxy group detected by IR and ^1H NMR were included in the calculation. The combined figure of merit (FOM) of the best set in $P1$ was 2.00; many interpeak distances were not adequate and the correct structure was not found. In the case of $P\bar{1}$, the FOM was 2.52, all the non-H atoms appeared and almost all the interpeak distances were reasonable. The refinements with $P\bar{1}$ were carried out by block-diagonal least squares on F (*UNICSIII*; Sakurai & Kobayashi, 1979) with anisotropic thermal parameters for non-H atoms. All the H atoms were located on the difference Fourier maps, refined isotropically; final $R = 0.052$ and $wR = 0.069$, $w = 1/[\sigma^2(|F_o|) + 0.0006(|F_o|)^2]$. There was no residual peak greater than $0.3 \text{ e}\text{\AA}^{-3}$; atomic parameter shifts were less than one fifth of their standard deviations. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All the calculations were performed on a HITAC M200H at The Institute for Molecular Science and a FACOM M360 at The Institute for Solid State Physics.

Table 1. Atomic parameters (positional parameters $\times 10^4$)

$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
O(1A)	11836 (2)	5538 (2)	107 (2)	3.2
O(1B)	6813 (2)	5572 (2)	-5034 (2)	3.2
N(1A)	11154 (2)	7031 (2)	-1432 (3)	2.9
N(2A)	9538 (3)	5590 (3)	2210 (3)	4.3
N(3A)	8065 (2)	6733 (2)	-960 (3)	3.2
N(4A)	7790 (3)	8303 (3)	-4442 (4)	5.5
N(1B)	6144 (2)	7080 (2)	-3202 (3)	2.9
N(2B)	4502 (3)	5599 (3)	-7104 (3)	4.6
N(3B)	3072 (2)	6735 (2)	-3697 (3)	3.2
N(4B)	2794 (3)	8375 (3)	53 (3)	5.2
C(1A)	10028 (3)	8073 (3)	-1672 (3)	2.9
C(3A)	10994 (3)	6477 (2)	-437 (3)	2.5
C(4A)	9761 (3)	6898 (3)	306 (3)	2.6
C(5A)	8889 (3)	7110 (2)	-1009 (3)	2.4
C(6A)	9045 (3)	7729 (3)	-2043 (3)	2.8
C(7A)	9708 (3)	8750 (3)	-92 (4)	3.3
C(8A)	9480 (3)	8100 (3)	1146 (4)	3.2
C(9A)	10227 (3)	8727 (3)	-2885 (4)	3.9
C(10A)	9660 (3)	6163 (3)	1381 (3)	2.9
C(11A)	8363 (3)	8040 (3)	-3374 (4)	3.5
C(12A)	10327 (4)	7919 (3)	2485 (4)	4.7
C(13A)	8187 (3)	8692 (3)	1736 (4)	4.4
C(14A)	13041 (3)	5165 (3)	-475 (5)	4.7
C(1B)	5012 (3)	8121 (3)	-2768 (3)	2.8
C(3B)	5978 (3)	6510 (3)	-4300 (3)	2.7
C(4B)	4730 (3)	6928 (3)	-4955 (3)	2.5
C(5B)	3884 (3)	7129 (3)	-3595 (3)	2.5
C(6B)	4043 (3)	7770 (3)	-2444 (3)	2.8
C(7B)	4670 (3)	8786 (3)	-4199 (4)	3.4
C(8B)	4425 (3)	8123 (3)	-5557 (3)	3.2
C(9B)	5246 (3)	8759 (3)	-1408 (4)	3.9
C(10B)	4631 (3)	6169 (3)	-6175 (3)	3.1
C(11B)	3359 (3)	8104 (3)	-1055 (3)	3.3
C(12B)	5247 (4)	7957 (3)	-6943 (4)	4.8
C(13B)	3112 (3)	8700 (3)	-6030 (4)	4.4
C(14B)	8028 (3)	5209 (3)	-4512 (5)	4.7

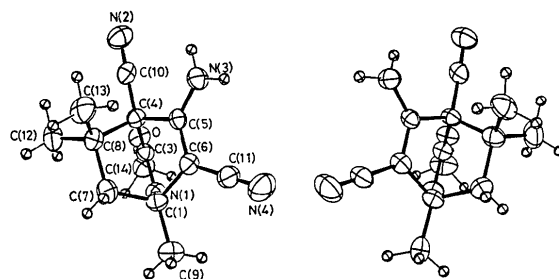


Fig. 1. Perspective views of molecules A (left) and B (right) (50% probability), with atom numbering, from the same direction.

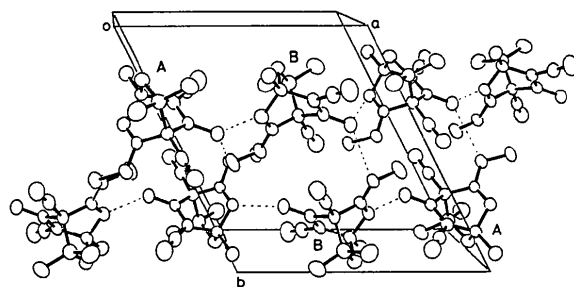


Fig. 2. Crystal structure along the c axis. Possible hydrogen bonds are shown with broken lines.

Table 2. Bond distances (Å) and angles (°) of possible hydrogen bonds (B...H—A)

These possible hydrogen bonds are shown in Fig. 2 with broken lines.

B...H—A	B...A	B...H	H—A	B...H—A
O(1A)...H1(N3A ⁱⁱ)—N(3A ⁱ)	3.132 (4)	2.24 (5)	1.01 (5)	147 (4)
O(1B)...H1(N3B ⁱⁱ)—N(3B ⁱ)	3.152 (4)	2.36 (4)	0.88 (4)	149 (4)
N(1A)...H2(N3B ⁱⁱⁱ)—N(3B ⁱⁱⁱ)	2.994 (4)	2.01 (4)	0.99 (4)	168 (3)
N(1B)...H2(N3A ⁱⁱⁱ)—N(3A ⁱⁱⁱ)	2.982 (4)	2.08 (4)	0.92 (4)	167 (4)

Symmetry code: none *x, y, z*; (i) 2 - *x*, 1 - *y*, - *z*; (ii) 1 - *x*, 1 - *y*, - 1 - *z*; (iii) 1 + *x, y, z*

Discussion. The atomic parameters are given in Table 1.* The unit cell contains two crystallographically independent molecules (labeled *A* and *B* in Fig. 2). *A* and *B* molecules have almost the same geometry, as seen in Fig. 1. All molecules are linked firmly to each other by hydrogen bonds in a zigzag manner (listed in Table 2 and shown with broken lines in Fig. 2). The molecular structure with atom numbering is shown in Fig. 1. The molecule adopts a bridged dihydropyridine skeleton with enamine form at C(5) rather than imine: two H atoms are bonded to N(3), and the short C(5)—C(6) length indicates its double-bond character. This compound loses about 30% of its weight at 410 K probably owing to release of 2-methylpropene, C₄H₈.

* Lists of structure factors, anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms and interatomic distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43590 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Selected bond distances (Å) of molecules *A* and *B*

	(A)	(B)
N(1)—C(3)	1.254 (5)	1.259 (4)
C(5)—N(3)	1.341 (5)	1.343 (5)
C(5)—C(6)	1.340 (5)	1.349 (5)
C(4)—C(8)	1.609 (5)	1.597 (5)
C(7)—C(1)	1.548 (4)	1.530 (5)
C(7)—C(8)	1.539 (5)	1.545 (5)

through retro-Diels—Alder reaction and yields 4-amino-2-methoxy-6-methylpyridine-3,5-dicarbonitrile. It is worth noting that C(4A)—C(8A) and C(4B)—C(8B), 1.609 (5) and 1.597 (5) Å, are significantly long and might be broken easily in the degradation process. The N(1)—C(3) bonds are shorter than the normal C=N double bond (Sandorfy, 1970) by 0.3 or 0.4 Å: they are 1.254 (5) Å in molecule *A* and 1.259 (4) Å in *B* (Table 3).

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Structure of *cis*-1,2-Diphenyl-2-tolylvinyl Acetate

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Abstract. C₂₃H₂₀O₂, *M_r* = 328.41, orthorhombic, *Pbca*, *a* = 13.121 (2), *b* = 30.181 (4), *c* = 9.291 (2) Å, *V* = 3679.3 Å³, *Z* = 8, *D_x* = 1.19 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 0.69 cm⁻¹, *T* = 293 K, *F*(000) = 1392, final *R* = 0.043 for 2426 unique reflections. The acetate group is in an anticlinal antiperiplanar conformation.

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The molecule as a whole has a propeller conformation. The bond lengths and angles are similar to those in other triarylvinyli-X systems. Relative to the *trans* isomer, the *cis* isomer of 1,2-diphenyl-2-tolylvinyl acetate has the higher melting point and tolyl-CH₃ ¹H NMR absorption at higher field.

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