

The Crystal Structure of Dicyano-1-methyl-3*H*-isoindoleninium Methylide

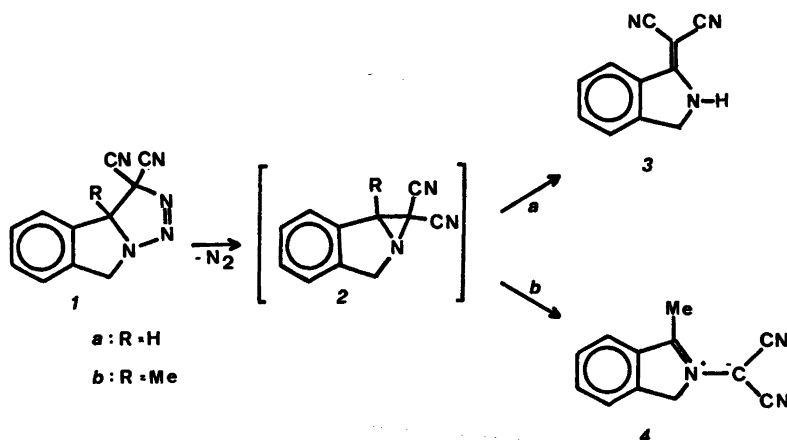
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The crystal structure of the title compound has been determined by X-ray methods using 1062 observed reflections obtained by counter methods. The crystals are monoclinic, space group $P2_1/c$, with four molecules per unit cell. The unit cell dimensions are: $a=10.075(4)$ Å; $b=10.564(4)$ Å; $c=10.191(4)$ Å; $\beta=117.05(3)^\circ$ at -160°C . The structure was solved by the use of the program assembly MULTAN and refined by full-matrix least-squares methods to a conventional R -factor of 0.039. Estimated standard deviations are 0.003 Å in distances and 0.2° in bond angles not involving hydrogen. The isoindolenine and dicyanomethine moieties are both planar with a dihedral angle of 30° about the connecting C—N bond of length 1.403 Å.

When the thermally unstable Δ^2 -1,2,3-triazoline *1a* decomposes at -15°C the isoindolinylidene-malononitrile *3* is formed (Scheme 1),¹ exhibit-

ing expected nitrile absorptions in IR, *viz.* at 2210 and 2218 cm^{-1} .² Decomposition of the homologous triazoline *1b* at room temperature gave a strongly coloured compound with IR absorptions at 2135 and 2180 cm^{-1} , indicating a highly conjugated system involving the nitrile groups. Corresponding IR absorptions (2130 and 2180 cm^{-1}) were found for pyridinium dicyanomethylide,³ and structure *4* was suggested for the decomposition product from *1b*.¹ Aziridines are found as products or intermediates in the thermolytic decomposition of Δ^2 -1,2,3-triazolines.⁴ If aziridine *2b* is an intermediate in the formation of *4*, this must involve a carbon—carbon bond cleavage. In view of this rather rare reaction route, the structure determination was judged to be of importance.



Scheme 1.

EXPERIMENTAL

Crystals were formed by recrystallization from methanol. The specimen used for the X-ray experiments was cut from a larger crystal to the approximate dimensions $0.5 \times 0.3 \times 0.1$ mm. Unit cell dimensions were calculated from diffractometer measurements of 15 general reflections using $\text{MoK}\alpha$ -radiation ($\lambda = 0.71069$ Å). Intensity data were recorded using a SYNTEX PI diffractometer with graphite crystal monochromated $\text{MoK}\alpha$ -radiation, the temperature at the crystal site was -160 °C. 1425 independent reflections with $\sin \theta/\lambda < 0.54$ Å⁻¹ were measured using the ω -scan technique, scan speed 3° min^{-1} . The scan range was 1.2° , background counts were taken for 8.4 s at each end of the scan. Three standard reflections measured after every 100 reflections showed no systematic variation during the experiment. 1062 reflections had net intensity larger than $2.5\sigma(I)$ and were regarded as observed; the remaining reflections were excluded from the calculations. The intensity data were corrected for Lorentz and polarization effects; no absorption or extinction corrections were applied. Atomic form factors used were those of Doyle and Turner⁵ for nitrogen and carbon, and of Stewart, Davidson and Simpson⁶ for hydrogen. A description of the computer programs employed is given in Ref. 7.

CRYSTAL DATA

Dicyano-1-methyl-3*H*-isoindoleninium methyliide, $\text{C}_{12}\text{H}_6\text{N}_3$, monoclinic, $a = 10.075(4)$ Å; $b = 10.564(4)$ Å; $c = 10.191(4)$ Å; $\beta = 117.05(3)^\circ$ ($t = -160$ °C). $V = 966.0$ Å³; $F(000) = 408$; $Z = 4$; $M = 195.22$; $D_x = 1.342$ g cm⁻³. Absent reflections: $(0k0)$ for k odd, $(h0l)$ for l odd. Space group $P2_1/c$ (No. 14).

STRUCTURE DETERMINATION

The positions of the heavy atoms were found using the program assembly MULTAN;⁸ hydrogen atomic positional parameters were calculated from stereochemical considerations. The refinement by full-matrix least-squares calculations [minimizing $\sum w(\Delta F)^2$] terminated with a conventional R value of 0.039, $R_w = 0.046$ and $S = [\sum w(\Delta F)^2/(n-m)]^{1/2}$ of 1.79.

Final parameters are given in Table 1, structural data are listed in Table 2. The structure factor listing may be obtained from the authors.

Estimated standard deviations as calculated from the correlation matrix are 0.003 Å in

Table 1. Fractional atomic coordinates and thermal parameters. The temperature factor is given by $\exp -2\pi^2(U_{11}a^2h^2 + \dots + 2U_{23}b^2c^2kl)$.

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23
N1	.1797(2)	.8880(2)	-.1962(2)	.021(1)	.020(1)	.025(1)	.001(1)	.008(1)	.000(1)
N2	-.1989(2)	.9620(2)	-.3403(2)	.027(1)	.040(1)	.046(1)	.000(1)	.012(1)	-.001(1)
N3	.0442(2)	.7748(2)	-.5516(2)	.037(1)	.041(1)	.033(1)	.001(1)	.013(1)	-.001(1)
C1	.3578(2)	.9232(2)	.0353(2)	.027(1)	.035(1)	.025(1)	-.008(1)	-.026(1)	.003(1)
C2	.4428(3)	.9753(3)	.1746(3)	.039(2)	.037(2)	.036(2)	-.003(1)	.014(1)	-.002(1)
C3	.5782(3)	.9164(3)	.2637(3)	.032(2)	.047(2)	.024(1)	-.013(1)	.002(1)	.003(1)
C4	.6253(3)	.8117(3)	.2165(3)	.032(2)	.044(2)	.039(2)	.002(1)	.011(1)	.008(1)
C5	.5396(3)	.7593(3)	.0786(3)	.028(2)	.043(2)	.036(2)	.002(1)	.011(1)	.007(1)
C6	.4048(3)	.8165(2)	-.0113(3)	.027(1)	.031(1)	.031(1)	-.001(1)	.010(1)	.003(1)
C7	.2906(3)	.7853(3)	-.1636(3)	.025(1)	.031(2)	.034(2)	.003(1)	.010(1)	.005(1)
C8	.2173(3)	.9665(2)	-.0841(2)	.030(1)	.026(1)	.030(1)	-.004(1)	.012(1)	.001(1)
C9	.1336(3)	1.0793(3)	-.0862(3)	.033(2)	.035(2)	.037(2)	.003(1)	.010(1)	-.003(1)
C10	.0478(2)	.8889(2)	-.3293(2)	.023(1)	.027(1)	.022(1)	.001(1)	.007(1)	.000(1)
C11	-.0865(3)	.9297(2)	-.3342(2)	.028(2)	.026(1)	.026(1)	-.003(1)	.007(1)	.000(1)
C12	.0470(2)	.8266(2)	-.4511(3)	.023(1)	.029(1)	.027(2)	.000(1)	.007(1)	.003(1)

Atom	X	Y	Z	B	Atom	X	Y	Z	B
H2	.400(2)	1.046(2)	.201(2)	.6(4)	H3	.636(3)	.954(2)	.357(3)	3.0(5)
H4	.727(3)	.768(3)	.282(3)	3.6(6)	H5	.576(3)	.677(3)	.048(3)	4.1(6)
H71	.328(3)	.784(2)	-.237(3)	2.8(5)	H72	.240(3)	.704(3)	-.174(3)	3.2(6)
H91	.202(3)	1.140(3)	-.010(3)	4.2(6)	H92	.049(4)	1.055(3)	-.068(3)	4.7(7)
H93	.089(3)	1.121(3)	-.187(4)	3.9(6)					

Table 2. Structural data. Estimated standard deviations are 0.003 Å in bond lengths and 0.2° in angles not involving hydrogen atoms.

Bond lengths (Å)		Corr.	Bond angles (°)		
N1-C8	1.320	1.322	N1-C8-C9	124.5	
N1-C7	1.482	1.485	N1-C8-C1	108.2	
N1-C10	1.402	1.403	C8-C1-C6	108.8	
C8-C9	1.455	1.457	C6-C1-C2	121.4	
C8-C1	1.458	1.460	C1-C2-C3	116.9	
C1-C2	1.395	1.397	C2-C3-C4	121.5	
C2-C3	1.395	1.396	C3-C4-C5	121.4	
C3-C4	1.374	1.377	C4-C5-C6	117.9	
C4-C5	1.387	1.389	C5-C6-C1	120.9	
C5-C6	1.384	1.386	C1-C6-C7	108.3	
C6-C1	1.387	1.391	C6-C7-C1	102.6	
C6-C7	1.489	1.490	C7-N1-C8	112.1	
C10-C11	1.399		C7-N1-C10	120.5	
C11-N2	1.157		C8-N1-C10	127.3	
C10-C12	1.402		N1-C10-C11	120.8	
C12-N3	1.150		N1-C10-C12	118.3	
			C11-C10-C12	119.8	
C-H (mean)	0.99(3)		C10-C11-N2	178.8	
			C10-C11-N3	178.9	
Deviation from LS planes (Å)			Torsional angles (°)		
1. N1	.018	C4	.033	C11-C10-N1-C8	-31.9
C8	-.001	C5	.029	C12-C10-N1-C8	159.8
C9	.067	C6	-.009	C11-C10-N1-C7	143.1
C1	-.038	C7	.001	C12-C10-N1-C7	-25.2
C2	-.052	C10	-.041	N1-C8-C9-H91	-157
C3	-.011			N1-C8-C9-H92	81
				N1-C8-C9-H93	-36
2. N1	-.044	C10	.084	C10-N1-C7-H71	61
N2	-.035	C11	.024	C10-N1-C7-H72	-54
N3	-.035	C12	.025		

Angle between 1 and 2 29.7°

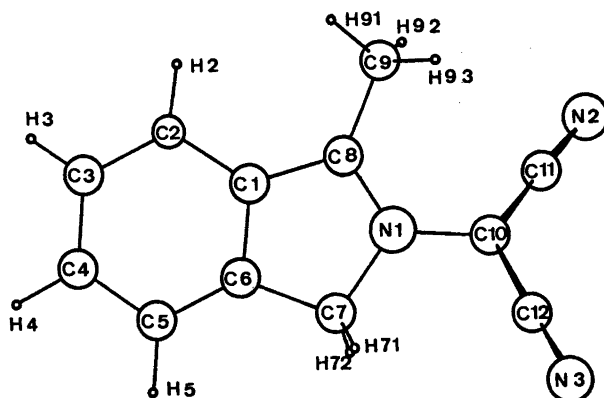


Fig. 1. The structure as seen normal to the least-squares plane through the isoindoleninium moiety.

bond lengths and 0.2° in angles not involving hydrogen atoms.

The thermal parameters for the 11 atoms of the molecule not including the cyano groups were analysed in terms of rigid-body motion. The r.m.s. ΔU was found to be $2.7 \times 10^{-3} \text{ \AA}^2$, and the results were used for correction of the corresponding bond lengths for libration.

A drawing of the molecule as projected on the isoindoline plane is presented in Fig. 1. The numbering of the atoms corresponds to that given in the tables.

DISCUSSION

The structure determination proves the decomposition product of the methyl homologue of *1* (Scheme 1) to be the *4* isomer.

The bond lengths and angles have expected values. The N1–C8 bond length corresponds to a bond order a little higher than that of the pyridine C–N bond; the geometry of the dicyanomethylide part corresponds within the experimental errors to that found in pyridinium dicyanomethylide.⁹

The molecule consists of two essentially planar parts, *i.e.* the methylisoindoleninium and the dicyanomethylide moieties. The angle between the least-squares planes is 29.7° . The pyridinium dicyanomethylide has been found to be nearly planar;⁹ the reason for the large dihedral angle in the present structure is to be found in the close proximity of the C11–N2 cyano group to the methyl group. The C9–C11 and C9–N2 separations are 2.95 and 3.40 Å, respectively, and the C11–H93 distance is 2.66 Å.

The packing of the molecules in the crystal shows no unusual features. Intermolecular separations are those to be expected for stacked aromatic molecules.

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REFERENCES

1. Kolsaker, P., Ellingsen, P. O. and Wøien, G. *Acta Chem. Scand. B* 32 (1978) 683.
2. Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, Chapman & Hall, London 1975.

3. Rieche, A. and Dietrich, P. *Chem. Ber.* 96 (1963) 3044.
4. Szeimies, G. and Huisgen, R. *Chem. Ber.* 99 (1966) 491; Broeck, W., Overbergh, N., Samyn, D., Smets, G. and L'Abbé, G. *Tetrahedron* 27 (1971) 3527; Logothetis, A. L. *J. Am. Chem. Soc.* 87 (1965) 749.
5. Doyle, P. A. and Turner, P. S. *Acta Crystallogr. A* 24 (1968) 390.
6. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
7. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
8. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* 27 (1971) 368.
9. Bugg, C. and Sass, R. L. *Acta Crystallogr.* 18 (1969) 591.

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