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The Crystal Structure of Pyridinium Dicyanomethylide, $C_8H_5N_3$

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The structure of pyridinium dicyanomethylide, $C_8H_5N_3$, has been determined by X-ray single-crystal diffraction techniques. The crystals are monoclinic in the space group $P2_1/m$, with two molecules per unit cell. The unit-cell constants are: $a=7{\cdot}87\pm0{\cdot}02$, $b=12{\cdot}512\pm0{\cdot}004$, $c=3{\cdot}86\pm0{\cdot}01$ Å, $\beta=114{\cdot}8°\pm0{\cdot}1°$. Atomic and thermal vibrational coordinates were refined by isotropic least-squares methods. The refined structure was found to be significantly non-planar.

Introduction

Stable carbanions have been known to exist for many years. Recently, a number of very interesting conjugated carbanions have been prepared by Dr. R. E. Benson and his associates at E. I. du Pont de Nemours Central Research Laboratory (Webster, Mahler & Benson, 1962). Dr. Benson has very kindly given us several samples of these compounds, and our investigations have been directed toward the determination of the bonding displayed by these conjugated systems. The structure of ammonium tricyanomethide, the first of these compounds to be investigated, has been reported (Desiderato & Sass, 1965). This paper reports the results of a structural study of pyridinium dicyanomethylide.

Experimental

The sample of $C_8H_5N_3$ was prepared by Linn, Webster and Benson of E. I. du Pont de Nemours (Linn, Webster & Benson, 1963). The crystals obtained from Dr. Benson were well formed yellow needles suitable for X-ray diffraction study. The crystal selected for investigation was approximately 0·3 mm in diameter and 2 mm in length.

The crystal was mounted along the needle axis. Rotation and Weissenberg photographs showed the Laue symmetry to be $2/m$ (C_{2h}). The space group was determined to be either $P2_1/m$ or $P2_1$ derived from the systematic absence $0k0$ absent if $k=2n+1$.

Choosing the needle axis as the c axis, the cell constants b and d_{100} were determined from a zero-layer Weissenberg photograph. The angle β was determined by the method of angular lag applied to the first and second layer Weissenberg photographs. The c axis was determined from a rotation photograph. The following values of the unit cell constants were obtained (Cu $K\alpha$ radiation; $\lambda=1{\cdot}5418$ Å):

$$a=7{\cdot}87\pm0{\cdot}02,\ b=12{\cdot}512\pm0{\cdot}004,\ c=3{\cdot}86\pm0{\cdot}01\ \text{Å}.$$
$$\beta=114{\cdot}8°+0{\cdot}1°.$$

Assuming two molecules per unit cell, the measured lattice constants yield a calculated density of 1·37 g.cm^{-3}. The observed density measured by volume displacement is 1·36 g.cm^{-3}.

Multiple film equi-inclination Weissenberg photographs of the $l=0$, 1, and 2 layers were taken with filtered Cu $K\alpha$ radiation. The intensities of the various reflections were estimated visually with a standard intensity strip. Interlayer correlation of intensities was made by comparison with a photograph which contained four-hour exposures of a 50° segment of each layer. The intensities were then corrected by the appropriate Lorentz, polarization and Tunell factors; absorption was neglected.

The structure determination

The space group was arbitrarily assumed to be $P2_1/m$, and this choice was verified by the structure determination.

The relatively short c axis (3·86 Å) and the anticipated planarity of the molecule suggested the probability of a well-defined [001] projection. The Patterson projection $P(u, v)$ was calculated from the relative intensities of the 70 observed $hk0$ reflections. For the unit cell to contain two molecules and the space group to be $P2_1/m$, it was apparent that the molecules must lie on crystallographic mirror planes. Assuming planar molecules situated across the mirror planes and perpendicular to the c axis, the positions of intramolecular vectors were compared with the observed Patterson function. Good agreement was found. Pursuing this assumption, the complete set of vectors between two molecules related by a center of symmetry was calculated. Only the x coordinate of the center of gravity of this vector set is affected by the location of the center of the molecule.

A scaled diagram of this intermolecular vector array was then superimposed on the Patterson projection. The x coordinate of the center of the array was varied until a reasonable overlay was found. The coordinates of the center of the vector set subsequently yielded the coordinates of the vector between the centers of mass of the two molecules. This procedure led directly to a set of trial positional parameters.

Table 1. *Observed and calculated structure factors for pyridinium dicyanomethylide*

h	k	F_{obs}	F_{calc}	h	k	F_{obs}	F_{calc}	h	k	F_{obs}	F_{calc}	h	k	F_{obs}	F_{calc}
		hk0													
1	0	20.34	-21.89	2	3	8.08	-7.97	-1	6	13.78	13.65	0	14	<0.79	-0.42
2	0	20.73	-21.56	3	3	14.41	13.96	-2	6	<1.34	1.08	1	14	<0.51	2.57
3	0	28.16	27.84	4	3	6.27	-5.46	-3	6	10.07	-10.24	-1	0	15.76	-16.96
4	0	14.14	-11.47	0	4	13.27	-12.65	-4	6	6.32	-6.09	-3	0	22.41	21.52
5	0	8.35	-8.80	1	4	7.12	7.75	-5	6	6.14	5.99	-4	0	41.86	-43.54
7	0	3.90	4.60	2	4	9.19	8.26	-6	6	<1.84	-2.76	-5	0	2.70	3.90
1	1	14.74	12.40	3	4	<1.55	-0.87	-7	6	3.04	-4.23	-6	0	2.59	3.45
2	1	22.43	22.66	4	4	14.10	15.42	-8	6	8.39	10.85	-7	0	10.58	-10.73
3	1	6.92	6.69	5	4	3.86	-4.61	-9	6	<0.90	-1.46	-8	0	3.83	3.11
4	1	7.61	5.89	0	5	16.58	-14.18	-1	7	3.38	-3.56	-9	0	<1.18	2.67
5	1	3.09	-2.94	1	5	<1.29	0.63	-2	7	4.35	3.96	-10	0	<0.67	-0.17
6	1	<2.24	-0.49	2	5	11.19	-12.07	-3	7	4.26	-3.99	-1	1	5.41	-5.90
8	1	3.70	4.08	3	5	4.15	-5.56	-4	7	5.58	5.59	-2	1	12.44	-11.15
0	2	35.43	-42.22	4	5	10.88	11.30	-5	7	<1.80	1.17	-3	1	11.29	-8.01
1	2	6.89	7.32	5	5	<1.84	0.16	-6	7	<1.84	1.33	-4	1	12.30	-10.49
2	2	18.63	-17.94	0	6	4.65	4.11	-7	7	3.90	4.26	-5	1	1.79	-0.17
3	2	3.83	-3.67	1	6	18.97	-15.41	-8	7	<1.36	-1.31	-6	1	5.11	4.67
4	2	10.72	10.72	2	6	2.27	1.94	-1	8	7.67	8.78	-7	1	<1.43	0.06
5	2	5.10	-5.60	3	6	4.13	3.13	-2	8	<1.61	1.51	-8	1	3.71	3.38
6	2	<2.25	0.27	4	6	19.17	-19.94	-3	8	4.87	-5.73	-9	1	<1.17	-0.57
1	3	21.11	-23.81	5	6	4.51	4.85	-4	8	2.58	2.27	-10	1	<0.65	-0.30
2	3	14.14	14.17	0	7	10.88	9.16	-5	8	<1.84	1.34	-1	2	1.17	-1.64
3	0	4.93	3.43	1	7	<1.53	-0.04	-6	8	3.09	-4.33	-2	2	7.40	8.78
4	3	11.93	-12.33	2	7	2.37	1.72	-7	8	<1.60	1.08	-3	2	11.02	-10.77
5	3	<2.08	0.96	3	7	4.93	4.78	-8	8	1.14	-1.54	-4	2	16.62	13.72
6	3	4.18	-5.36	4	7	6.03	-5.87	-1	9	5.76	5.62	-5	2	1.82	-1.24
7	3	<2.21	1.81	5	7	<1.77	-0.87	-2	9	10.88	-13.39	-6	2	5.11	5.03
0	4	16.50	-15.92	0	8	2.90	-0.99	-3	9	<1.78	1.51	-7	2	4.26	2.97
1	4	2.31	-2.53	1	8	<1.66	-0.67	-4	9	3.29	-4.36	-8	2	2.64	-2.72
2	4	24.93	24.19	2	8	5.62	6.83	-5	9	<1.83	-2.93	-9	2	<1.15	2.13
3	4	5.60	-4.80	3	8	<1.80	-0.39	-6	9	4.08	4.83	-10	2	<0.58	-0.14
4	4	4.66	4.29	4	8	2.17	1.86	-7	9	<1.45	-1.71	-1	3	1.40	-0.87
5	4	9.08	10.66	5	8	<1.68	-1.91	-8	9	<0.94	-0.25	-2	3	4.94	-5.51
6	4	4.83	-5.25	6	8	<1.35	3.45	-1	10	5.95	-6.44	-3	3	12.04	13.25
7	4	2.59	-1.67	0	9	5.07	-4.56	-2	10	2.18	-3.11	-4	3	2.09	1.24
1	5	15.96	-15.63	1	9	<1.76	-1.20	-3	10	3.16	3.65	-5	3	5.14	-6.45
2	5	11.40	-10.90	2	9	9.05	9.57	-4	10	3.09	3.58	-6	3	6.66	6.47
3	5	13.99	12.01	3	1	4.04	-3.36	-5	10	<1.77	-0.39	-7	3	<1.44	2.04
4	5	<1.98	-1.86	4	9	<1.77	-1.12	-6	10	2.82	3.66	-8	3	2.83	-3.47
5	5	3.48	-4.11	6	9	1.94	-0.77	-7	10	<1.25	-0.49	-9	3	<1.11	2.20
6	5	14.44	17.86	0	10	5.00	-4.76	-1	11	6.25	-6.23	-10	3	0.96	-2.63
7	5	2.57	-2.91	1	10	<1.83	0.00	-2	11	16.17	18.99	-1	4	8.21	7.88
0	6	5.76	-2.63	2	10	2.89	-3.48	-3	11	2.95	-2.85	-2	4	19.08	-17.98
1	6	6.55	6.01	3	10	<1.80	1.86	-4	11	2.14	-1.71	-3	4	<0.99	0.01
2	6	9.09	-6.83	4	10	2.36	2.23	-5	11	4.81	5.66	-4	4	6.49	5.48
3	6	3.67	-2.57	5	10	<1.38	0.55	-6	11	2.04	-2.84	-5	4	4.62	3.22
4	6	7.86	-8.60	0	11	4.53	-3.95	-7	11	<0.96	-1.55	-6	4	7.28	-6.28
5	6	4.10	-4.71	1	11	5.27	5.67	-1	12	<1.81	1.68	-7	4	<1.44	1.73
6	6	4.73	5.38	2	11	4.81	-5.22	-2	12	1.97	1.75	-8	4	<1.34	-1.19
7	6	<2.01	-0.65	3	11	3.24	-2.38	-3	12	<1.74	-0.24	-9	4	5.29	-4.90
8	6	<1.46	1.66	4	11	1.18	1.20	-4	12	2.30	-1.83	-1	5	16.87	-14.52
1	7	3.26	2.19	5	11	<1.14	2.05	-5	12	<1.45	-1.08	-2	5	3.52	3.16
2	7	5.86	4.33	0	12	2.34	2.59	-6	12	<1.14	-1.38	-3	5	8.11	7.59
3	7	6.19	-4.63	1	12	2.10	2.48	-1	13	1.94	2.20	-4	5	2.64	2.26
4	7	<2.17	-1.76	2	12	<1.68	0.98	-2	13	4.26	-4.29	-5	5	5.42	-4.36
5	7	2.67	2.26	3	12	2.48	-2.19	-3	13	<1.58	1.45	-6	5	8.10	-6.25
6	7	9.63	-9.29	4	12	<1.26	1.79	-4	13	<1.43	-1.97	-7	5	2.99	2.63
7	7	<1.88	2.10	5	12	<0.67	-1.09	-5	13	<1.19	-1.02	-8	5	<1.29	-1.98
8	7	<1.23	-0.25	0	13	1.97	-2.49	-6	13	<1.82	0.69	-9	5	3.78	-4.16
0	8	6.96	8.22	1	13	<1.61	-0.29	-1	14	1.61	-1.94	-1	6	2.06	-1.14
1	8	3.62	-3.05	2	13	<1.49	1.37	-2	14	<1.43	0.09	-2	6	9.65	6.65
2	8	9.59	9.23	3	13	<1.28	-1.48	-3	14	2.56	1.62	-3	6	<1.20	-0.66
3	8	<2.13	0.37	4	13	<0.89	1.39	-4	14	<1.12	-2.93	-4	6	<1.28	0.91
4	8	4.00	-4.71	0	14	1.79	2.45	-5	14	<0.66	0.05	-5	6	5.85	-5.05
5	8	5.33	5.12	1	14	<1.36	-0.89	-1	15	<1.14	-0.30	-6	6	3.85	1.85
6	8	<2.11	-0.93	2	14	2.80	-2.44	-2	15	2.62	-2.54	-7	6	<1.40	0.44
7	8	<1.71	-1.27	3	14	<0.88	0.76	-3	15	<0.92	-1.03	-8	6	2.06	2.41
8	8	<0.76	0.59	0	15	4.40	4.80					-9	6	3.99	3.20
1	9	10.10	10.27	1	15	1.94	-2.03			**bk2**		-1	7	9.09	6.21
2	9	<2.14	1.59	2	15	<0.62	0.91					-2	7	2.46	-0.89
3	9	3.93	-2.47	-1	0	5.18	6.38					-3	7	<1.30	-0.42
4	9	5.50	6.63	-2	0	13.99	14.07	0	0	15.02	14.90	-4	7	<1.36	0.13
5	9	<2.21	-0.46	-3	0	1.18	3.52	1	0	9.40	9.41	-5	7	<1.42	1.13
6	9	<1.96	-1.83	-4	0	15.65	-17.13	0	1	2.13	-1.07	-6	7	4.30	3.43
7	9	<1.47	-0.99	-5	0	5.34	-4.95	1	1	8.95	6.63	-7	7	<1.35	-0.59
0	10	19.89	-21.81	-6	0	4.09	-3.00	0	2	15.02	-15.19	-8	7	<1.13	-0.09
1	10	5.11	4.47	-7	0	<1.84	1.59	1	2	7.82	6.67	-9	7	1.87	2.54
2	10	<2.24	0.38	-8	0	<1.75	0.58	2	2	2.76	-1.14	-1	8	2.88	1.79
3	10	4.55	-5.51	-9	0	<1.39	1.98	3	2	3.69	-2.46	-2	8	8.51	-6.57
4	10	5.48	6.62	-1	1	19.63	23.74	0	3	14.16	13.38	-3	8	5.14	4.66
5	10	<2.09	0.77	-2	1	68.51	-75.65	1	3	<1.10	0.76	-4	8	5.89	-4.84
6	10	<1.78	-1.20	-3	1	5.23	7.20	2	3	4.43	4.84	-5	8	2.64	1.44
7	10	<1.12	-0.77	-4	1	2.36	2.63	3	3	4.83	-4.84	-6	8	3.73	-3.83
2	11	4.84	-5.17	-5	1	12.85	-13.43	0	4	3.40	-2.30	-7	8	<1.27	-1.18
3	11	<2.25	-2.03	-6	1	6.35	6.21	1	4	8.59	-8.34	-8	8	1.79	1.68
4	11	<2.14	-1.78	-7	1	<1.84	2.44	2	4	13.79	12.63	-1	9	4.00	2.27
5	11	<1.90	1.68	-8	1	<1.74	-0.70	3	4	2.97	2.97	-2	9	2.30	-1.46
6	11	<1.47	0.20	-9	1	<1.38	-1.65	0	5	<0.72	-1.03	-3	9	8.31	-7.85
0	12	14.95	14.19	-1	2	25.08	-27.20	1	5	2.17	1.95	-4	9	3.73	-3.65
1	12	3.49	-3.44	-2	2	6.74	-6.52	2	5	22.66	-20.76	-5	9	3.70	3.60
2	12	2.37	-1.14	-3	2	12.44	14.71	3	5	8.80	7.87	-6	9	<1.34	0.01
3	12	4.98	4.10	-4	2	<1.27	-1.87	4	5	5.57	4.71	-7	9	<1.15	-1.61
4	12	<1.94	-2.33	-5	2	2.25	-2.30	0	6	9.57	8.19	-8	9	2.46	3.38
5	12	<1.99	-0.92	-6	2	6.39	7.59	1	6	<1.32	0.45	-1	10	4.21	3.20
6	12	<1.01	-0.00	-7	2	<1.84	-1.29	2	6	14.41	-12.83	-2	10	2.43	-1.94
1	13	2.27	1.86	-8	2	<1.73	0.61	3	6	<1.44	0.94	-3	10	8.68	-7.45
2	13	<2.05	-0.89	-9	2	<1.34	1.33	4	6	3.76	-2.40	-4	10	15.15	13.35
3	13	<1.91	0.96	-1	3	2.20	-3.21	0	7	3.14	2.59	-5	10	<1.36	-1.24
4	13	3.30	1.95	-2	3	3.41	-4.20	1	7	2.94	-1.09	-6	10	<1.23	0.47
5	13	<1.01	-1.37	-3	3	1.80	-1.21	2	7	12.68	10.35	-7	10	3.88	4.00
0	14	<1.92	1.30	-4	3	16.27	17.49	3	7	4.21	-4.86	-1	11	<1.40	1.65
1	14	<1.88	0.83	-5	3	2.25	-2.57	0	8	6.33	6.56	-2	11	3.76	3.40
2	14	5.81	-4.66	-6	3	2.71	-2.15	1	8	7.17	-5.07	-3	11	3.09	2.05
3	14	<1.58	1.26	-7	3	5.56	7.88	2	8	3.12	2.29	-4	11	3.89	3.84
4	14	<1.23	-0.09	-8	3	<1.70	-1.21	3	8	3.07	2.40	-5	11	<1.25	0.32
1	15	<1.52	-0.51	-9	3	<1.29	-1.23	0	9	5.29	-4.91	-6	11	2.97	-2.36
2	15	3.32	3.16	-1	4	<1.01	2.90	1	9	<1.44	1.00	-7	11	0.00	0.08
3	15	<1.06	-0.86	-2	4	1.46	-1.43	2	9	3.16	2.59	-1	12	3.57	-2.34
0	16	0.96	-1.23	-3	4	<1.22	-1.68	3	9	<1.28	0.76	-2	12	2.78	1.67
		hk1		-4	4	12.13	12.27	4	9	6.66	-5.60	-3	12	5.73	4.68
				-5	4	2.08	-1.51	0	10	7.98	-7.99	-4	12	10.13	-9.01
				-6	4	2.23	-2.18	1	10	<1.40	0.01	-5	12	2.24	1.57
0	0	32.96	32.96	-7	4	<1.82	3.40	2	10	3.82	2.37	-6	12	<0.84	0.19
1	0	18.86	15.02	-8	4	7.01	-8.82	3	10	<1.16	0.52	-1	13	<1.13	-1.38
0	1	11.92	13.12	-9	4	<1.21	1.21	0	11	<1.37	0.08	-2	13	<1.14	0.40
1	1	21.87	-19.36	-1	5	1.73	1.82	1	11	2.99	-2.94	-3	13	2.17	-1.70
2	1	21.14	17.33	-2	5	3.92	3.81	2	11	1.87	0.33	-4	13	<1.01	-0.92
3	1	5.69	5.18	-3	5	6.11	6.63	3	11	<0.98	-0.30	-5	13	<0.82	0.73
0	2	3.11	-3.09	-4	5	7.82	-6.55	0	12	2.99	2.93	-1	14	3.26	-2.15
1	2	4.94	1.78	-5	5	<1.67	-0.16	1	12	2.40	0.89	-2	14	5.95	4.33
2	2	17.21	-14.69	-6	5	5.01	-6.09	2	12	<1.00	-0.05	-3	14	<0.84	-0.71
3	2	2.25	1.26	-7	5	4.70	-5.84	0	13	2.59	-1.66	-4	14	<0.66	-0.70
0	3	34.41	32.81	-8	5	<1.58	2.45	1	13	2.06	1.31				
1	3	11.82	-9.61	-9	5	<1.09	-0.40	2	13	<0.70	-2.73				

Table 2. *Final atomic parameters*

Atom	x	y	z	β	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(\beta)$
C(1)	0·9574	0·2500	1·0984	3·68	0·0023	0·0000	0·0048	0·36
C(2)	0·8703	0·3458	0·9364	3·40	0·0015	0·0008	0·0034	0·23
C(3)	0·6980	0·3456	0·6206	2·97	0·0014	0·0008	0·0032	0·22
C(4)	0·4441	0·2500	0·1413	2·33	0·0019	0·0000	0·0042	0·28
C(5)	0·3594	0·3475	−0·0340	2·89	0·0014	0·0008	0·0033	0·21
N(1)	0·6163	0·2500	0·4640	1·88	0·0015	0·0000	0·0033	0·21
N(2)	0·2893	0·4243	−0·1782	4·12	0·0013	0·0007	0·0027	0·21

The trial positional parameters were used in an isotropic least-squares refinement of the *hk*0 data. A total of 70 observed reflections were used. All reflections were equally weighted in the refinement. The reliability index R decreased from 29·9% to 11·5%. The largest atomic parameter change was a shift of 0·006 in the x coordinate of C(4).

Trial z parameters were obtained by tilting the molecule with respect to the [001] plane in a manner which would compensate for the observed distortion in the projected pyridine ring. The z parameter of the center of gravity was adjusted to give a reasonable packing and to position the molecule in a manner which would account for the large intensity of the $\bar{2}11$ reflection of ($F_{obs}=68{\cdot}51$).

A total of 325 observed reflections were used to refine the atomic parameters and individual atom isotropic temperature factors. The program employed was one written for the Rice Computer. Form factors were obtained from *International Tables for X-ray Crystallography* (1962). A table look-up and linear interpolation was employed. All reflections were assigned equal weights in the refinement. The complete normal equation matrix was used in the solution. The final overall R value obtained was 12·9%. The final calculated and observed structure factors are listed in Table 1. Included in this listing are the minimum observable structure factors and the corresponding calculated values for the unobserved reflections. The unobserved data was not included in the refinement of parameters. A summary of the final atomic parameters and their estimated standard deviations is presented in Table 2.

Discussion of the structure

The dimensions of $C_8H_5N_3$ are presented in Table 3. The C–C and C–N bond lengths displayed by the pyridinium ring are equivalent to bond lengths reported for pyridine (De More, Wilcox & Goldstein, 1954). The value of 1·42 Å for the C(4)–N(1) bond length is not significantly different from what one would expect for a single C(sp^2) – N(sp^2) bond. The value of 1·13 Å for the C(5)–N(2) bond distance is sligthly shorter than a normal C–N triple bond. Within experimental error, the bond angles appear to be normal.

To determine the non-planarity of the molecule, the atomic parameters were converted to an orthogonal coordinate system with axes a, b and c sin β. With these orthogonal atomic coordinates, a least-squares plane was fitted to C(4) and the atoms constituting the pyridinium ring. The equation of the plane is $1{\cdot}3047\ x-0{\cdot}9769\ z-3{\cdot}7441=0$. The atoms deviate from the plane as follows:

C(1) ---------- 0·001 Å above plane
C(2) ---------- 0·001 Å below plane
C(3) ---------- 0·010 Å above plane
N(1) ---------- 0·007 Å below plane
C(4) ---------- 0·003 Å above plane
C(5) ---------- 0·082 Å below plane
N(2) ---------- 0·130 Å below plane .

The C(4)–C(5)–N(2) unit thus makes an angle of 3° with respect to this plane. The 3° non-planarity has also been reported for the tricyanomethide carbanion (Desiderato & Sass, 1964). It appears therefore that this non-planarity is real and that C(4) possesses a significant amount of negative charge. Fig. 1 shows a diagram of the structure projected onto the (001) plane; Fig. 2 shows the projection on the (010) plane. There are no abnormally short intermolecular distances displayed in the crystal. The shortest intermolecular

Table 3. *Interatomic dimensions in* $C_8H_5N_3$

Distances		Angles	
C(1)–C(2)	1·39 ± 0·01 Å	C(2′)–C(1)–C(2)	118° 56′ ± 1°
C(2)–C(3)	1·39 ± 0·01	C(1)–C(2)–C(3)	120 29 ± 1
C(4)–C(5)	1·41 ± 0·01	C(2)–C(3)–N(1)	119 27 ± 1
C(3)–N(1)	1·37 ± 0·01	C(3)–N(1)–C(3′)	120 16 ± 1
C(4)–N(1)	1·42 ± 0·01	N(1)–C(4)–C(5)	120 1 ± 1
C(5)–N(2)	1·13 ± 0·01	C(3)–N(1)–C(3′)	120 16 ± 1
		C(5′)–C(4)–C(5)	119 22 ± 1
		C(4)–C(5)–N(2)	180 0 ± 1
		C(3)–N(1)–C(4)	119 21 ± 1

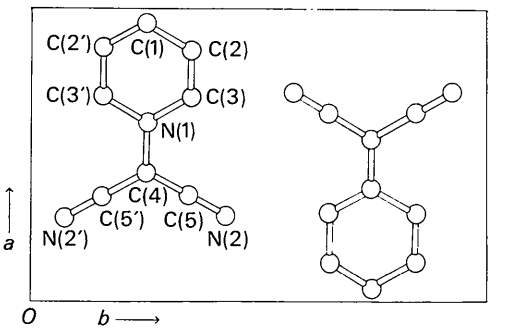

Fig. 1. Projection of the pyridinium dicyanomethylide structure down [001].

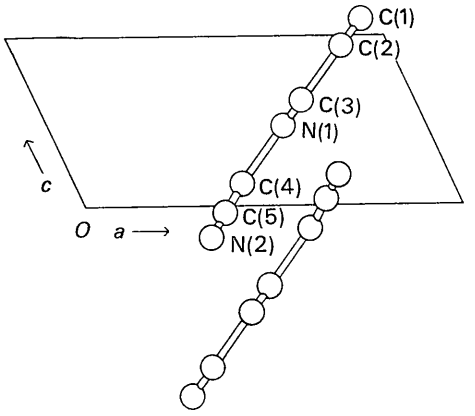

Fig. 2. Projection of the pyridinium dicyanomethylide structure down [010].

distance is 3·37 Å distance between C(3) and N(2) of molecules related by a center of symmetry.

The authors intend to attempt the synthesis and structural determination of *p*-nitropyridinium dicyanomethylide. It is hoped that introduction of the nitro group will offer an opportunity to observe the effect of increased conjugation upon the planarity of the carbanion.

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The Crystal Structure of Ternary Silicides ThM_2Si_2 (M=Cr, Mn, Fe, Co, Ni and Cu)

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The existence of well defined and isomorphous ternary phases of the general composition ThM_2Si_2 (M=Cr, Mn, Fe, Co, Ni and Cu) has been established in the corresponding intermetallic systems. The crystal structure of the isomorphous series of compounds has been determined by the X-ray powder method. The compounds crystallize in the tetragonal system in the space group $I4/mmm$ (D_{4h}^{17}) as determined from the systematically absent reflexions. The unit cells containing two formula units of ThM_2Si_2, have the dimensions: $ThCr_2Si_2$, $a=4{\cdot}043\pm0{\cdot}001$, $c=10{\cdot}577\pm0{\cdot}002$ Å; $ThMn_2Si_2$, $a=4{\cdot}021\pm0{\cdot}001$, $c=10{\cdot}493\pm0{\cdot}002$ Å; $ThFe_2Si_2$, $a=4{\cdot}038\pm0{\cdot}003$, $c=9{\cdot}820\pm0{\cdot}005$ Å; $ThCo_2Si_2$, $a=4{\cdot}015\pm0{\cdot}003$, $c=9{\cdot}760\pm0{\cdot}005$ Å; $ThNi_2Si_2$, $a=4{\cdot}076\pm0{\cdot}001$, $c=9{\cdot}551\pm0{\cdot}002$ Å; $ThCu_2Si_2$, $a=4{\cdot}104\pm0{\cdot}001$, $c=9{\cdot}864\pm0{\cdot}002$ Å.

Introduction

The investigation of the phase relations in the system Th–Mo–Si (Sikirica, 1963) revealed the existence of a compound of the composition close to $ThMo_2Si_2$ with a very complex powder diffraction pattern. The oscillation photographs of a single-crystal fragment showed that the cell is tetragonal with the lattice parameters: $a=4{\cdot}01$ and $c\simeq87{\cdot}5$ Å. Graphical indexing by means of Bunn charts suggested that a pseudocell, with the parameter c approximately eight times as small, could be chosen for the rough description of the structure. In order to examine the influence of the electronic structure and radii of transition metals upon the formation of such structures, we have investigated the effect of the replacement of molybdenum by chromium, manganese, iron, cobalt, nickel and copper. All of them led to the formation of a new compound of the exact stoichiometric composition ThM_2Si_2. The unit cell in all these cases has almost the same dimen-

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