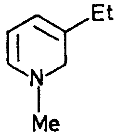
Crystal Structures of 3-Ethyl- and 5-Ethyl-1,2-dihydro-1-methylpyridine(tricarbonyl)chromium

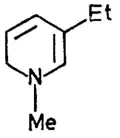
By **Cedric A. Bear** and **James Trotter,*** Department of Chemistry, University of British Columbia, Vancouver 8, British Columbia, Canada

Crystals of the 3-ethyl-complex (III) are orthorhombic, $a = 14{\cdot}999(7)$, $b = 13{\cdot}263(5)$, $c = 12{\cdot}164(9)$ Å, $Z = 8$, space group *Pbca*, those of the 5-ethyl-complex (IV) are monoclinic, $a = 10{\cdot}700(3)$, $b = 14{\cdot}280(6)$, $c = 7{\cdot}926(3)$ Å, $\beta = 97{\cdot}83(4)°$, $Z = 4$, space group $P2_1/n$. The structures were determined from diffractometer data by Patterson and Fourier methods, and refined by full-matrix least-squares techniques to R 0·039 (III; 916 reflections) and 0·067 (IV; 907 reflections). The chromium atom is bonded to the two double bonds and nitrogen atom of the six-membered ring in both compounds, to give a distorted octahedral co-ordination.

DIHYDROPYRIDINES play an important role as intermediates in various biological systems, as instanced by the role of 1,4-dihydropyridine in oxidation–reduction reactions involving NADH. Electron-withdrawing groups stabilize the dihydropyridine systems and there has been extensive investigation of such compounds.[1] As yet, however, little is known about dihydropyridines without these substituents. As part of an investigation of a series of these compounds, 3-ethyl- (I) and 5-ethyl-1,2-dihydro-1-methylpyridine (II) have been prepared[2] and stabilized by formation of complexes [(III) and (IV)] with $Cr(CO)_3$. In view of the interest in these compounds, X-ray crystal analyses of the chromium complexes have been undertaken.



(I)



(II)

EXPERIMENTAL

Crystals of both compounds are red plates with (010) developed. Unit-cell and space-group data were determined from film and diffractometer measurements.

Crystal Data.—(III), $C_{11}H_{13}CrNO_3$, $M = 259{\cdot}2$, Orthorhombic, $a = 14{\cdot}999(7)$, $b = 13{\cdot}263(5)$, $c = 12{\cdot}164(9)$ Å, $U = 2420(2)$ Å^3, $Z = 8$, $D_c = 1{\cdot}42$, $\mu(\text{Mo-}K_\alpha) = 9{\cdot}8$ cm^{-1}. Space group *Pbca* (No. 61).

(IV), $C_{11}H_{13}CrNO_3$, $M = 259{\cdot}2$, Monoclinic, $a = 10{\cdot}700(3)$, $b = 14{\cdot}280(6)$, $c = 7{\cdot}926(3)$ Å, $\beta = 97{\cdot}83(4)°$, $U = 1199{\cdot}6(8)$ Å^3, $Z = 4$, $D_c = 1{\cdot}43$, $\mu(\text{Mo-}K_\alpha) = 9{\cdot}9$ cm^{-1}. Space group $P2_1/n$ (No. 14).

The intensities of the reflections were measured on a Datex-automated General Electric XRD 6 diffractometer with Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å). With $2\theta \leqslant 45°$, 1924 reflections were measured for (III) and 1854 for (IV). Of these, 916 (III) and 907 (IV) had intensities $I > 3\sigma(I)$, where $\sigma^2(I) = S + B + (0{\cdot}03S)^2$ and S is the scan count and B the background count. The remaining reflections in both compounds were classified as unobserved. Lorentz and polarization factors were applied but no absorption corrections were made.

Structure Analysis.—For both compounds the position of the chromium atom was determined from a three-dimensional Patterson function and the carbon, nitrogen, and oxygen atoms from subsequent electron-density maps. The structures were refined by full-matrix least-squares methods. The function minimized was $\Sigma w(F_o - F_c)^2$ with w adjusted to give best constancy of average values of $w(F_o - F_c)^2$. The weighting scheme used was $\sqrt{w} = F^*/F_o$ when $F_o \geqslant F^*$; and $\sqrt{w} = F_o/F^*$ when $F_o < F^*$; for (III) F^* 35·0 and for (IV) F^* 15·5. After refinement of the heavy atom with anisotropic thermal parameters and the light atoms with isotropic temperature factors difference-Fourier syntheses were calculated from which the hydrogen atoms were located. Refinement was then continued with the light atoms assuming anisotropic thermal parameters and the hydrogen atoms included but not refined. Further difference syntheses showed no large maxima. For (III) the final R was 0·039, the weighted R being 0·050, for the 916 observed reflections. These values for (IV) were 0·067 and 0·076 respectively for the 907 observed reflections. Measured and calculated structure factors for both complexes are listed in Supplementary Publication No. SUP 20781 (19 pp., 1 microfiche).† Positional and thermal parameters are listed in Table 1, bond lengths and angles in Table 2. The mean value of the carbon–hydrogen lengths is 0·96 Å. The structures of the molecules are shown in Figures 1—4, together with the crystallographic atom numbering system.

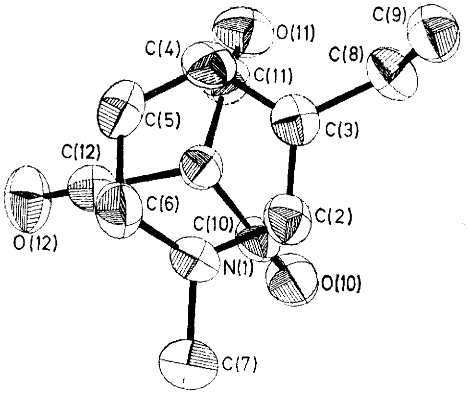


FIGURE 1 The structure of (III), a view of the molecule perpendicular to the planar portion of the dihydropyridine ring

DISCUSSION

The conjugated nature of the dienamine system of both six-membered rings is clearly shown by the bond lengths,

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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[1] U. Eisner and J. Kuthan, *Chem. Rev.*, 1972, **72**, 1.

[2] C. A. Bear, W. R. Cullen, J. P. Kutney, V. E. Ridaura, J. Trotter, and A. Zanarotti, *J. Amer. Chem. Soc.*, 1973, **95**, 3058.

the carbon–carbon double bonds ranging from 1·364 [C(5)–C(6) in (III)] to 1·397 Å [C(2)–C(3) in (IV)], longer than the normal value of 1·337 Å, while the central carbon–carbon lengths are 1·446 [(C4)–C(5) in (III)] and 1·426 Å [C(3)–C(4) in (IV)], and are thus shorter than normal. The C(sp^2)–N lengths of 1·401 [N(1)–C(6) in (III)] and 1·405 Å [N(1)–C(2) in (IV)] are also shorter than normal.

In *N*-benzyl-1,4-dihydronicotinamide,[3] the dihydronicotinamide ring is planar, but in (III) and (IV) the six-membered rings are not planar (see Table 3), in agreement with the situation found in tricarbonyl(1,2-dihydro-1,4-dimethylpyridine)chromium (V).[4] While in the latter compound it is apparently only the methylene carbon which does not lie in the plane of the other five atoms, the present study shows that not only do the methylene carbon atoms deviate significantly, but the carbon atoms next to them are also displaced from the plane of the other four atoms. These displacements are in the direction opposite to the metal atom, and suggest

TABLE 1

Atomic positions (× 10^4) and anisotropic thermal parameters (× 10^4). Hydrogen atoms have isotropic temperature factors of 5·0 Å^2

(*a*) (III)

	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cr	1267(1)	1215(1)	2523(1)	30·7(5)	45·3(6)	70·1(7)	2·0(5)	1·9(5)	9·0(7)
O(10)	3114(3)	979(4)	1632(4)	44(3)	118(5)	112(5)	12(3)	25(3)	5(4)
O(11)	1487(4)	3458(4)	2295(5)	76(4)	49(3)	167(7)	3(3)	−1(3)	20(4)
O(12)	472(4)	1275(5)	279(5)	95(4)	128(6)	108(5)	−20(4)	−45(4)	38(5)
N(1)	948(3)	−291(4)	3004(4)	41(2)	44(3)	70(4)	−7(2)	0(3)	0(4)
C(2)	1619(4)	−388(4)	3889(5)	44(3)	48(4)	71(5)	0(3)	1(3)	6(4)
C(3)	1867(4)	687(5)	4174(5)	43(3)	50(4)	57(5)	0(3)	−2(3)	8(4)
C(4)	1179(5)	1359(5)	4323(5)	68(4)	55(4)	65(5)	−2(4)	15(4)	−4(4)
C(5)	305(4)	1128(5)	3890(6)	43(4)	67(5)	102(6)	12(4)	32(4)	8(5)
C(6)	200(4)	309(6)	3224(6)	34(3)	70(5)	103(7)	0(4)	17(4)	10(6)
C(7)	813(5)	−1207(6)	2347(6)	64(4)	69(5)	110(7)	−16(4)	−9(4)	−6(5)
C(8)	2820(5)	860(5)	4578(6)	70(5)	64(5)	91(6)	−14(4)	−27(4)	17(5)
C(9)	3104(5)	1963(6)	4645(7)	77(5)	76(5)	132(9)	−19(5)	−22(5)	17(6)
C(10)	2393(5)	1062(5)	1960(5)	45(4)	60(4)	58(4)	0(3)	−1(4)	5(4)
C(11)	1392(4)	2598(5)	2399(6)	37(3)	61(5)	96(6)	8(3)	0(4)	16(5)
C(12)	770(5)	1227(6)	1141(6)	46(4)	72(6)	89(6)	−11(4)	−12(4)	17(5)

	x/a	y/b	z/c		x/a	y/b	z/c
H(2a)	2135	−763	3566	H(7c)	634	−1737	2648
H(2b)	1385	−737	4569	H(8a)	3199	513	4034
H(4)	1243	1960	4654	H(8b)	2825	452	5251
H(5)	−181	1543	4009	H(9a)	2728	2175	5113
H(6)	−282	167	2919	H(9b)	3747	1891	4926
H(7a)	484	−987	1736	H(9c)	3057	2382	3823
H(7b)	1221	−1284	2068				

(*b*) (IV)

	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cr	1612(1)	2502(1)	1992(2)	81(1)	44(1)	138(2)	11(1)	22(1)	−2(2)
O(10)	1134(7)	2010(6)	−1712(9)	117(8)	117(6)	141(13)	4(6)	21(8)	−29(7)
O(11)	−148(8)	913(6)	2357(10)	151(10)	68(5)	289(19)	−12(6)	67(11)	8(8)
O(12)	3876(7)	1245(5)	2628(10)	119(8)	72(5)	277(18)	41(6)	−10(9)	−22(7)
N(1)	2475(6)	3828(5)	1841(9)	74(7)	45(4)	169(14)	−5(4)	31(8)	−4(6)
C(2)	1165(8)	3954(6)	1444(12)	84(9)	43(5)	182(16)	12(6)	24(10)	−3(8)
C(3)	411(9)	3671(6)	2658(12)	89(9)	39(5)	157(17)	6(5)	18(10)	−18(8)
C(4)	1008(9)	3244(6)	4184(12)	101(10)	54(5)	165(19)	15(6)	53(12)	−12(8)
C(5)	2303(9)	3245(7)	4543(12)	115(11)	53(5)	141(19)	17(6)	−10(11)	−2(8)
C(6)	3031(9)	3929(8)	3628(12)	80(9)	71(7)	170(20)	3(7)	−5(11)	−1(9)
C(7)	3257(9)	4156(8)	571(14)	110(11)	80(7)	227(23)	−5(8)	45(13)	22(10)
C(8)	−1007(9)	3797(7)	2311(13)	80(10)	54(6)	224(23)	6(6)	36(12)	11(9)
C(9)	−1424(8)	4670(7)	3274(12)	90(10)	59(6)	225(21)	9(6)	26(12)	11(9)
C(10)	1338(8)	2202(7)	−293(12)	79(9)	63(7)	154(19)	11(5)	34(11)	−15(8)
C(11)	535(10)	1525(8)	2266(13)	107(11)	54(6)	161(21)	7(7)	20(11)	1(9)
C(12)	3013(9)	1721(7)	2368(11)	103(11)	47(5)	148(18)	3(6)	29(11)	−20(8)

The scattering factor for an atom is expressed as: $f_0 \exp - (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)$.

	x/a	y/b	z/c		x/a	y/b	z/c
H(2)	785	4260	383	H(7c)	4153	3746	1194
H(4)	500	2987	4764	H(8a)	−1296	3347	2760
H(5)	2692	3027	5510	H(8b)	−1199	3806	1020
H(6a)	2986	4598	3770	H(9a)	−1162	5024	2415
H(6b)	3839	3865	3365	H(9b)	−2299	4678	2972
H(7a)	2878	3939	−349	H(9c)	−1291	4549	4643
H(7b)	3333	4828	625				

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[3] I. L. Karle, *Acta Cryst.*, 1961, **14**, 497.

[4] G. Huttner and O. S. Mills, *Chem. Ber.*, 1972, **105**, 3924.

that the conjugation in (V) is more pronounced than in (III) and (IV). Consideration of the bond lengths in (V) gives some support to this, as the lengths of the carbon–carbon double bonds (1·382 and 1·384 Å) are, in general, slightly longer than in (III) and (IV) while the central carbon–carbon bond (1·407 Å) and the *sp*² carbon–nitrogen bond (1·386 Å) are somewhat shorter. However, these differences are, in most instances, within the limits of error.

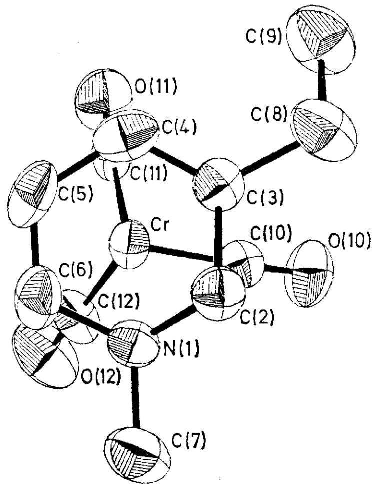

FIGURE 2 The structure of (IV) viewed as in Figure 1

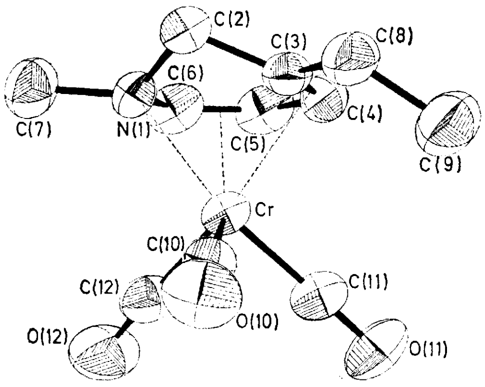

FIGURE 3 A view of (III)

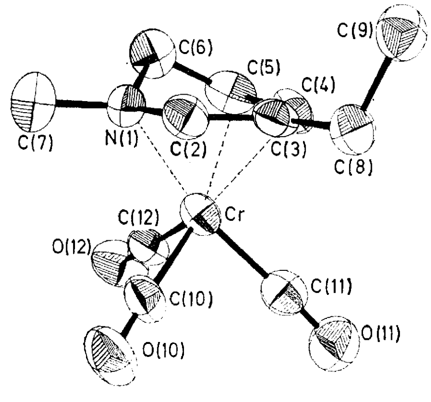

FIGURE 4 A view of (IV)

In (III) and (IV) the interaction between the chromium atom and the dihydropyridine ring is through the lone-pair electrons of the nitrogen and the π-electrons of the two double bonds. This gives a distorted octahedral geometry to the metal atoms, as would be expected from the short distances between the co-ordinating points of the six-membered ring. The distances to the centres of the double bonds are, for (III): Cr–C(3)C(4), 2·149 and Cr–C(5)C(6), 2·082; and for (IV): Cr–C(2)C(3) 2·072, and Cr–C(4)C(5), 2·153 Å.

TABLE 2

Distances (Å) and angles (°.)

(*a*) (III)

(i) Distances

Cr–N(1)	2·136(5)	O(12)–C(12)	1·142(8)
Cr–C(2)	2·750(6)	N(1)–C(2)	1·479(8)
Cr–C(3)	2·310(6)	N(1)–C(6)	1·401(8)
Cr–C(4)	2·202(6)	N(1)–C(7)	1·468(9)
Cr–C(5)	2·205(6)	C(2)–C(3)	1·514(8)
Cr–C(6)	2·175(6)	C(3)–C(4)	1·376(9)
Cr–C(10)	1·835(7)	C(3)–C(8)	1·528(9)
Cr–C(11)	1·837(7)	C(4)–C(5)	1·446(10)
Cr–C(12)	1·838(8)	C(5)–C(6)	1·364(9)
O(10)–C(10)	1·158(7)	C(8)–C(9)	1·525(10)
O(11)–C(11)	1·169(8)		

(ii) Angles

C(10)–Cr–C(11)	89·1(3)	C(2)–C(3)–C(8)	116·5(5)
C(10)–Cr–C(12)	91·9(3)	C(4)–C(3)–C(8)	124·2(6)
C(11)–Cr–C(12)	87·6(3)	C(3)–C(4)–C(5)	119·7(6)
C(2)–N(1)–C(6)	117·1(5)	C(4)–C(5)–C(6)	119·3(6)
C(2)–N(1)–C(7)	114·7(5)	N(1)–C(6)–C(5)	118·3(6)
C(6)–N(1)–C(7)	117·1(6)	C(3)–C(8)–C(9)	115·0(6)
N(1)–C(2)–C(3)	104·6(5)	Cr–C(10)–O(10)	178·0(6)
C(2)–C(3)–C(4)	117·1(6)	Cr–C(11)–O(11)	178·1(7)
		Cr–C(12)–O(12)	117·1(7)

(b) (IV)

(i) Distances

Cr–N(1)	2·117(7)	O(12)–C(12)	1·142(10)
Cr–C(2)	2·159(9)	N(1)–C(2)	1·405(11)
Cr–C(3)	2·215(9)	N(1)–C(6)	1·467(11)
Cr–C(4)	2·206(8)	N(1)–C(7)	1·470(12)
Cr–C(5)	2·314(10)	C(2)–C(3)	1·397(13)
Cr–C(6)	2·757(10)	C(3)–C(4)	1·426(13)
Cr–C(10)	1·845(9)	C(3)–C(8)	1·515(13)
Cr–C(11)	1·841(12)	C(4)–C(5)	1·376(13)
Cr–C(12)	1·860(10)	C(5)–C(6)	1·497(14)
O(10)–C(10)	1·149(10)	C(8)–C(9)	1·558(13)
O(11)–C(11)	1·147(11)		

(ii) Angles

C(10)–Cr–C(11)	85·5(4)	C(2)–C(3)–C(8)	119·9(9)
C(10)–Cr–C(12)	92·0(4)	C(4)–C(3)–C(8)	121·8(9)
C(11)–Cr–C(12)	91·7(4)	C(3)–C(4)–C(5)	119·8(9)
C(2)–N(1)–C(6)	117·7(7)	C(4)–C(5)–C(6)	118·4(8)
C(2)–N(1)–C(7)	116·7(8)	N(1)–C(6)–C(5)	103·5(7)
C(6)–N(1)–C(7)	115·8(7)	C(3)–C(8)–C(9)	110·6(8)
N(1)–C(2)–C(3)	117·4(8)	Cr–C(10)–O(10)	178·2(8)
C(2)–C(3)–C(4)	118·3(8)	Cr–C(11)–O(11)	176·8(9)
		Cr–C(12)–O(12)	178·9(8)

In tricarbonyl(π-cyclohexadienyl)manganese [5] the carbonyl groups are orientated so that the carbon atoms lie directly below atoms of the ring. However, in the

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[5] M. R. Churchill and F. R. Scholer, *Inorg. Chem.*, 1969, **8**, 1950.

present compounds as well as in (V)[4] the $Cr(CO)_3$ is rotated from such a position, so that the carbon atoms of the carbonyl groups lie slightly to one side of positions *directly* below atoms of the ring (see Figures 1 and 2). The direction of rotation is such that it would increase the overlap of the metal orbitals and the π-orbitals of the double bond.

TABLE 3

Mean planes, where X, Y, and Z are co-ordinates in Å referred to orthogonal axes, *a*, *b*, and *c**, and deviations (Å) of atoms from the planes

(*a*) (III)

Plane (1): N(1), C(2)—(6)

$$0{\cdot}384X + 0{\cdot}463Y - 0{\cdot}799Z + 2{\cdot}753 = 0$$

N(1) 0·201, C(2) −0·332, C(3) 0·196, C(4) 0·067, C(5) −0·158, C(6) −0·074

Plane (2): N(1), C(4)—(6)

$$0{\cdot}200X + 0{\cdot}560Y - 0{\cdot}804Z + 2{\cdot}871 = 0$$

N(1) −0·001, C(4) 0·003, C(5) −0·006, C(6) 0·006, Cr 1·684, O(10) 2·930, O(11) 3·638, O(12) 3·686, C(2) −0·739, C(3) −0·145, C(7) −0·080, C(8) −0·128, C(9) 0·710, C(10) 2·457, C(11) 2·862, C(12) 2·895

(*b*) (IV)

Plane (1): N(1), C(2)—(6)

$$0{\cdot}129X - 0{\cdot}930Y - 0{\cdot}343Z + 5{\cdot}442 = 0$$

N(1) 0·176, C(2) −0·059, C(3) −0·132, C(4) 0·085, C(5) 0·161, C(6) −0·388

Plane (2): N(1), C(2)—(4)

$$-0{\cdot}003X - 0{\cdot}901Y - 0{\cdot}433Z + 5{\cdot}621 = 0$$

N(1) −0·003, C(2) 0·010, C(3) −0·011, C(4) 0·006, Cr 1·680, O(10) 3·575, O(11) 3·657, O(12) 3·011, C(5) −0·157, C(6) −0·753, C(7) −0·023, C(8) −0·011, C(9) −1·445, C(10) 2·843, C(11) 2·879, C(12) 2·513

The major difference in the two compounds is in the orientation of the ethyl groups; that of (III) is such that of the terminal carbon atom of the ethyl group is on the same side of the ring as the chromium atom while that of (IV) lies on the opposite side (see Figures 3 and 4). Also, C(8) of (IV), being attached to one of the middle atoms of the diene system, lies in the plane of N(1), C(2)—(4), while in (III) C(8) does not lie in the analogous plane. This difference in orientation appears to be sufficient to alter the packing of the molecules and as such causes the two compounds to crystallize in different space groups. Intermolecular distances correspond to van der Waals interactions and the packing of the molecules is shown in Figures 5 and 6.

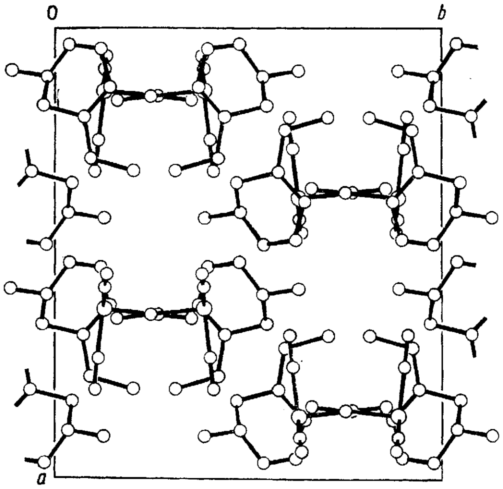

FIGURE 5 Projection of the unit cell of (III) along *c*

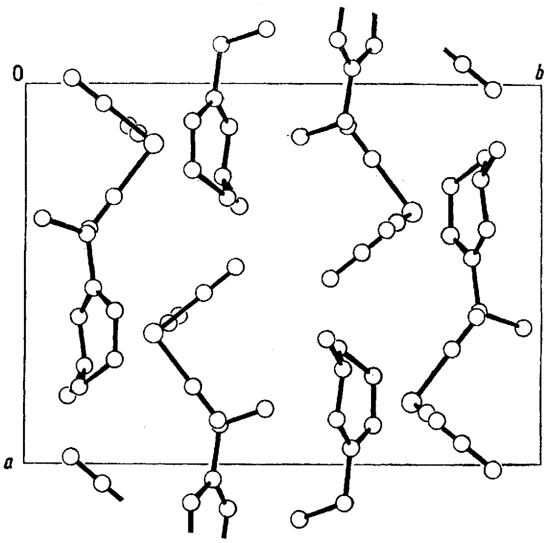

FIGURE 6 Projection of the unit cell of (IV) along *c**

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[3/676 *Received, 2nd April*, 1973]