Crystal and Molecular Structure of Dicarbonyl{hydrotris(pyrazol-1-yl)-borato-*N*(2),*N*(2)′,*N*(2)″}-π-(2-methylallyl)molybdenum

By **Elizabeth M. Holt** * and **Smith L. Holt**, Chemistry Department, University of Wyoming, Laramie, Wyoming 82070
Kenneth J. Watson, Department of Physical Chemistry, Chemical Laboratory IV, H. C. Ørsted Institute, DK 2100 Copenhagen Ø, Denmark

The crystal and molecular structure of the title compound has been determined from three-dimensional single-crystal *X*-ray diffraction data measured by counter techniques. Crystals are monoclinic, space group $P2_1/a$, with $Z = 4$ in a unit cell of dimensions: $a = 15{\cdot}735(10)$, $b = 12{\cdot}885(5)$, $c = 9{\cdot}343(4)$ Å, and $\beta = 111{\cdot}95(4)°$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares methods to R 3·3% for 3325 non-zero independent reflections. The co-ordination sphere of the molybdenum atom in each molecule consists of one nitrogen from each of the three pyrazolyl rings of the pyrazolylborate ligand, two carbon atoms from the σ-bonded carbonyl groups, and a π-2-methylallyl group.

AMONG the many pyrazolylborato-molybdenum compounds whose syntheses and physical properties have been reported,[1-5] three containing a multicentre-bonded group have recently been subjected to *X*-ray structure investigation. π-Allyldicarbonyl[dihydrobis-(3,5-dimethyl-1-pyrazolyl)borato]molybdenum [6] and dicarbonylcycloheptatrienyl[dihydrobis-(3,5-dimethyl-1-pyrazolyl)borato]molybdenum,[7] which involve bidentate bispyrazolylborate ligands, each have their molybdenum atom in a slightly distorted octahedral environment through co-ordination to two carbonyl groups, two nitrogen atoms from the pyrazolylborate ligand, a two-electron, three-centre bond, and an interaction with a proton on the boron atom. Each has a very short Mo–B distance and, as a consequence of this and the proton involvement, a chelate ring in strained boat form. The structure of π-cyclopentadienyltetrakis-(1-pyrazolyl)-boratomolybdenum has recently been the subject of a preliminary [8] and a detailed [9] study. In this compound, the molybdenum atom is co-ordinated to two of the four pyrazolyl rings of tetrakis(1-pyrazolyl)borate, to two carbonyl groups, and to the C_5H_5 ring through a four-electron, five-centre bond. There is a high degree of crowding around the molybdenum atom, as evidenced by the many non-bonded distances to this atom of <3 Å and by the relatively large degree of tilt of the cyclopentadienyl ring.[9] This present study of dicarbonyl[hydrotris(1-pyrazolyl)borato]-π-(methylallyl)molybdenum [3] was undertaken to provide information about a molybdenum–pyrazolylborate compound in which the molybdenum atom forms a multicentre bond without the crowding of either additional non-bonded pyrazolyl groups or of 3,5-dimethyl substitution, and without the strain on the chelate ring introduced when the molybdenum is involved with a proton on the boron atom.

The high-temperature n.m.r. data for this material show the three pyrazolyl groups to be equivalent while the low-temperature limiting spectrum indicates that two of the groups are identical and different from the third. Trofimenko interpreted these observations as an indication that at higher temperatures rotation of the tridentate ligand takes place about the Mo–B axis whereas at lower temperatures rotation is hindered, one pyrazolyl group existing in an environment different from that of the other two.[3] It was hoped that a structural study would confirm or disprove this hypothesis in the expectation that the low-temperature solution species should resemble the crystalline molecule.

EXPERIMENTAL

Crystal Data.—$C_{15}H_{17}BMoN_6O_2$, $M = 420{\cdot}1$, Monoclinic, $a = 15{\cdot}735(10)$, $b = 12{\cdot}885(5)$, $c = 9{\cdot}343(4)$ Å, $\beta = 111{\cdot}95(4)°$, $U = 1756{\cdot}9$ Å^3, $D_m = 1{\cdot}60(3)$ (by flotation), $Z = 4$, $D_c = 1{\cdot}59(3)$, $F(000) = 848$. Space group $P2_1/c$ from systematic absences $= h0l$ for $h = 2n$, $0k0$ for $k = 2n$. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å, μ(Mo-K_α) $=$ 7·66 cm^{-1}.

Preliminary Weissenberg and precession photographs established the space group. A platelet of dimensions 0·40 × 0·21 × 0·50 mm was mounted on a Picker four-circle automated diffractometer. Graphite-monochromated molybdenum-K_α radiation was used for data collection. The *X*-ray tube take-off angle was 4°. During alignment procedures more accurate unit-cell dimensions were determined by least-squares fit of the angular positions of 12 independent, relatively high-angle reflections. All independent reflections to $\sin\theta_{\max.} = 0{\cdot}69$ were sampled by the θ—2θ scan procedure, the 2θ scan being at 1° min^{-1} over a basic range of 2·6° extended to allow for a dispersion $\Delta\lambda/\lambda = 0{\cdot}592$. Background measurements were made for 20 s each on either side of the diffracted peak. Three standard reflections were measured after every 40 reflections, and their intensities were constant to within 5% over the whole data measurement period. Of the 5165 reflections measured, 3325 were classed as observed $[|F_o|/\sigma(|F_o|) > 1{\cdot}5$ where $|F_o|$ is the observed structure amplitude and $\sigma|F_o|$ is its corresponding estimated standard deviation] after subtraction of background and correction for Lorentz and polarization factors. No absorption corrections were applied.

Determination of the Structure and Refinement.—The

---

[1] S. Trofimenko, *Inorg. Chem.*, 1969, **8**, 2675.

[2] S. Trofimenko, *J. Amer. Chem. Soc.*, 1968, **90**, 4754.

[3] S. Trofimenko, *J. Amer. Chem. Soc.*, 1969, **91**, 588.

[4] S. Trofimenko, *J. Amer. Chem. Soc.*, 1969, **91**, 3183.

[5] S. Trofimenko, *Inorg. Chem.*, 1970, **9**, 2493.

[6] C. A. Kosky, P. Ganis, and G. Avitabile, *Acta Cryst.*, 1971, **B27**, 1859.

[7] F. A. Cotton, J. L. Calderon, M. Jeremic, and A. Shaver, *J.C.S. Chem. Comm.*, 1972, **13**, 777.

[8] J. L. Calderon, F. A. Cotton, and A. Shaver, *J. Organometallic Chem.*, 1972, **38**, 105.

[9] E. M. Holt and S. L. Holt, *J.C.S. Dalton*, 1973, 1893.

position of the molybdenum atom in the unit cell was located from a Patterson synthesis. Three cycles of least-squares refinement of a scale factor and the molybdenum atom's position and isotropic temperature parameter gave R 0·233. A difference-Fourier synthesis based upon the molybdenum atom's contribution to the phases then showed the positions of the remaining 24 atoms. After three cycles of full-matrix least-squares refinement of these positions, individual atomic isotropic thermal parameters and the scale factor, R was 10·4%. A difference-Fourier map plotted at this stage indicated the presence of thermal anisotropic motion and so the isotropic temperature factors were converted to their anisotropic equivalents. Refinement of these together with the other parameters for three further full-matrix least-squares cycles gave R 3·3%. The maximum ratio of the shift of a parameter to its corresponding estimated standard deviation was 0·03 so no further refinement was undertaken. No attempt was made to locate hydrogen atoms. A final difference-Fourier map showed no peak $>0·3$ eÅ^{-3}. Unit weights for all reflections were used until the final cycles of refinement when a weighting scheme to reduce the weight of the high-intensity observations was introduced. In this scheme unit weights were retained for reflections with $|F_o| \leqslant 30·0$ and weights of $(30·0/|F_o|)^2$ were applied to those of greater intensity. This choice seemed justified by the fact that at the conclusion of the analysis, the values of $\langle\Sigma(|F_o| - |F_c|)^2\rangle$ for the reflections grouped in 20 sets of increasing $|F_o|$ did not differ by more than a factor of 2·6.

TABLE 1

Atomic co-ordinates with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Mo	0·29595(2)	0·30618(2)	0·82494(3)
O(1)	0·1483(3)	0·3755(4)	0·9521(5)
O(2)	0·3613(3)	0·5321(2)	0·9223(4)
N(1)	0·2259(2)	0·1543(2)	0·7076(3)
N(2)	0·2115(2)	0·1374(2)	0·5560(3)
N(3)	0·2034(2)	0·3659(2)	0·5990(3)
N(4)	0·1926(2)	0·3191(2)	0·4617(3)
N(5)	0·3846(2)	0·2794(2)	0·6828(3)
N(6)	0·3468(2)	0·2352(2)	0·5395(3)
C(1)	0·2019(3)	0·3476(3)	0·9039(5)
C(2)	0·3389(3)	0·4480(3)	0·8866(4)
C(3)	0·1847(3)	0·0751(3)	0·7497(5)
C(4)	0·1443(3)	0·0072(3)	0·6271(6)
C(5)	0·1625(3)	0·0492(3)	0·5062(5)
C(6)	0·1484(3)	0·4501(3)	0·5636(5)
C(7)	0·1023(3)	0·4577(3)	0·4043(5)
C(8)	0·1324(3)	0·3734(3)	0·3441(4)
C(9)	0·4724(3)	0·2971(3)	0·7066(5)
C(10)	0·4927(3)	0·2628(3)	0·5796(5)
C(11)	0·4112(3)	0·2251(3)	0·4770(4)
C(12)	0·3105(3)	0·2180(4)	0·0515(4)
C(13)	0·3922(3)	0·2102(3)	0·0208(4)
C(14)	0·4383(3)	0·3068(3)	0·0353(4)
C(15)	0·4281(3)	0·1108(3)	0·9773(6)
B	0·2425(3)	0·2160(3)	0·4607(4)

The structure analysis and refinement described were carried out first on an XDS Sigma 7 computer with modifications of programs written by W. R. Busing, K. O. Martin, and M. A. Levy, and W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, and later on an IBM 360/75 computer using the programs of Stewart, Kundell, and Baldwin.[10] The X-ray atomic scattering factors used were taken from refs. 11 and 12. The real part of the anomalous scattering contribution for molybdenum was included.

DISCUSSION OF THE STRUCTURE

Final atomic co-ordinates are given in Table 1, anisotropic temperature factors in Table 2, and interatomic distances and angles in Tables 3 and 4. Final

TABLE 2

Atomic temperature factors in the form
$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{13}hl + 2\beta_{23}kl + 2\beta_{12}hk)]$
with estimated standard deviations in parentheses

Atom	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Mo	273(2)	347(2)	632(3)	7(1)	162(2)	−33(2)
	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
O(1)	57(2)	112(4)	198(6)	9(2)	70(3)	−36(4)
O(2)	73(2)	41(2)	148(5)	−10(2)	48(3)	−23(2)
N(1)	24(2)	33(2)	82(3)	−2(1)	18(2)	2(2)
N(2)	24(2)	34(2)	87(4)	−3(1)	21(2)	−15(2)
N(3)	25(1)	31(2)	74(3)	2(1)	16(2)	1(2)
N(4)	23(2)	44(2)	67(3)	2(1)	10(2)	2(2)
N(5)	22(2)	40(2)	74(3)	−2(1)	17(2)	−8(2)
N(6)	24(2)	37(2)	73(3)	1(1)	20(2)	−4(2)
C(1)	38(2)	58(3)	104(5)	−1(2)	32(3)	−17(3)
C(2)	39(2)	41(2)	78(4)	−1(2)	25(2)	−8(2)
C(3)	34(2)	39(2)	134(6)	−3(2)	31(3)	13(3)
C(4)	43(2)	38(2)	173(7)	−13(2)	43(3)	−10(3)
C(5)	32(2)	42(2)	149(6)	−9(2)	33(3)	−29(3)
C(6)	31(2)	36(2)	120(5)	7(2)	21(2)	9(2)
C(7)	37(2)	51(2)	116(5)	10(2)	11(3)	21(3)
C(8)	28(2)	58(2)	86(4)	4(2)	4(2)	17(3)
C(9)	24(2)	56(3)	109(5)	−3(2)	20(2)	−7(3)
C(10)	30(2)	55(2)	128(6)	3(2)	36(3)	4(3)
C(11)	33(2)	39(2)	100(4)	4(2)	37(2)	6(2)
C(12)	51(3)	75(3)	65(4)	−5(2)	22(3)	16(3)
C(13)	38(2)	45(2)	66(4)	−1(2)	3(2)	10(2)
C(14)	38(2)	54(2)	80(4)	−4(2)	−2(2)	1(3)
C(15)	44(2)	45(2)	144(6)	12(2)	−2(3)	10(3)
B	24(2)	42(2)	68(4)	−3(1)	16(2)	−10(2)

TABLE 3

Some interatomic distances (Å), with estimated standard deviations in parentheses

Mo–C(1)	1·959(6)	Mo · · · B	3·391(4)
Mo–C(2)	1·958(4)	C(12)–C(13)	1·421(8)
Mo–N(1)	2·312(3)	C(13)–C(14)	1·421(6)
Mo–N(3)	2·207(3)	C(13)–C(15)	1·515(7)
Mo–N(5)	2·283(4)	N(3) · · · C(2)	2·932(4)
Mo–C(12)	2·337(5)	N(3) · · · C(1)	2·868(6)
Mo–C(13)	2·258(4)	N(3) · · · O(1)	3·713(4)
Mo–C(14)	2·364(4)	N(3) · · · O(2)	3·777(6)
C(1)–O(1)	1·151(7)	C(6) · · · C(1)	3·249(6)
C(2)–O(2)	1·150(5)	C(6) · · · C(2)	3·391(4)
N(1)–N(2)	1·366(4)	C(6) · · · O(1)	3·755(5)
N(1)–C(3)	1·343(6)	C(6) · · · O(2)	3·896(5)
C(3)–C(4)	1·392(6)	N(1) · · · C(1)	3·198(6)
C(4)–C(5)	1·376(8)	N(1) · · · C(2)	4·249(4)
C(5)–N(2)	1·355(5)	N(1) · · · O(1)	4·113(6)
N(5)–N(6)	1·369(4)	N(1) · · · O(2)	5·391(3)
N(5)–C(9)	1·335(6)	C(3) · · · C(1)	3·712(5)
C(9)–C(10)	1·410(7)	C(3) · · · C(2)	5·318(4)
C(10)–C(11)	1·371(5)	C(3) · · · O(1)	4·437(4)
C(11)–N(6)	1·351(6)	C(3) · · · O(2)	6·453(6)
N(3)–N(4)	1·370(4)	N(5) · · · C(1)	4·093(7)
N(3)–C(6)	1·350(5)	N(5) · · · C(2)	3·144(5)
C(6)–C(7)	1·394(6)	N(5) · · · O(1)	5·355(6)
C(7)–C(8)	1·386(7)	N(5) · · · O(2)	4·044(5)
C(8)–N(4)	1·348(5)	C(9) · · · C(1)	5·272(5)
N(2)–B	1·543(6)	C(9) · · · C(2)	3·696(6)
N(4)–B	1·545(5)	C(9) · · · O(1)	6·405(7)
N(6)–B	1·547(5)	C(9) · · · O(2)	4·349(5)

---

[10] J. M. Stewart, F. A. Kundell, and J. C. Baldwin, 'X-Ray '63' System of Programs, 1970 version, University of Maryland Technical Report, TR-192.

[11] F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.

[12] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, pp. 202—203.

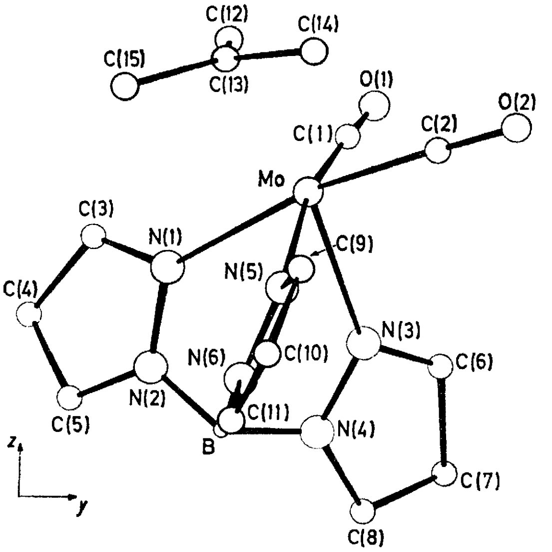
observed and calculated structure factors are listed in Supplementary Publication No. SUP 20763 (7 pp.).*

TABLE 4

Some bond angles (°), with estimated standard deviations in parentheses

Mo–C(1)–O(1)	177·3(4)	Mo–N(5)–N(6)	119·7(2)
Mo–C(2)–O(2)	177·8(4)	C(9)–N(5)–N(6)	106·1(3)
C(1)–Mo–N(3)	86·8(2)	N(5)–C(9)–C(10)	110·6(3)
C(2)–Mo–N(3)	89·3(1)	C(9)–C(10)–C(11)	104·6(4)
N(5)–Mo–N(3)	79·9(1)	C(10)–C(11)–N(6)	108·7(4)
N(1)–Mo–N(3)	79·3(1)	C(11)–N(6)–N(5)	109·9(3)
C(1)–Mo–C(13)	77·5(1)	C(11)–N(6)–B	127·8(3)
C(2)–Mo–C(13)	77·3(2)	N(5)–N(6)–B	121·8(3)
N(5)–Mo–C(13)	89·0(2)	Mo–N(3)–N(4)	123·3(2)
N(1)–Mo–C(13)	88·7(1)	N(4)–N(3)–C(6)	106·3(3)
C(1)–Mo–N(1)	83·4(2)	N(3)–C(6)–C(7)	110·4(4)
C(1)–Mo–C(2)	82·0(2)	C(6)–C(7)–C(8)	105·0(4)
C(2)–Mo–N(5)	95·4(2)	C(7)–C(8)–N(4)	108·6(3)
N(5)–Mo–N(1)	83·3(2)	C(8)–N(4)–N(3)	109·8(3)
C(13)–Mo–N(3)	165·6(2)	N(3)–N(4)–B	119·9(2)
Mo–N(1)–N(2)	119·4(4)	C(8)–N(4)–B	130·2(3)
C(3)–N(1)–N(2)	105·8(3)	C(12)–C(13)–C(14)	112·7(4)
N(1)–C(3)–C(4)	111·0(4)	C(12)–C(13)–C(15)	124·8(4)
C(3)–C(4)–C(5)	104·9(4)	C(15)–C(13)–C(14)	122·5(4)
C(4)–C(5)–N(2)	108·3(4)	N(2)–B–N(4)	106·8(3)
C(5)–N(2)–N(1)	110·0(4)	N(4)–B–N(6)	108·1(3)
N(1)–N(2)–B	121·9(3)	N(6)–B–N(2)	109·8(3)
C(5)–N(2)–B	127·9(3)		

The molecular conformation viewed down the crystallographic *a* axis is shown in the Figure. The molybdenum atom achieves an eighteen-electron configuration through co-ordination to two carbonyl groups, one nitrogen atom from each pyrazolyl ring of the terdentate pyrazolylborate group and the two-electron three-centre bond of the 2-methylallyl group.



The molecular conformation as viewed down the *a* axis

The geometry about the molybdenum atom is distorted octahedral. C(1), C(2), N(1), and N(5) are coplanar within 0·02 Å but the molybdenum is 0·23 Å above that plane. The central atom of the methyl allyl group, C(13), is 2·46 Å above that plane and N(3) is 1·96 Å below it (Table 5). The C(13)–Mo–N(3) angle is 165·6°.

The molybdenum–nitrogen distances range from 2·207 to 2·312 Å, similar to those observed in other compounds of this type. Likewise, the boron–nitrogen distances of 1·543—1·547 Å are not unusual. Co-ordination about the boron atom is roughly tetrahedral.

Although the molybdenum–carbon–oxygen bonds are slightly nonlinear [177·3(4) and 177·8(4)°], the small deviations from linearity almost certainly arise from the effects of local packing forces and have no further chemical significance.

TABLE 5

Equations of least-squares planes through atoms and deviations (Å) of atoms from the planes

Plane (1):

C(1), C(2), N(1), N(2) $0{\cdot}522x - 0{\cdot}569y + 0{\cdot}606z = 0{\cdot}457$

[C(1) −0·020, C(2) 0·020, N(1) 0·016, N(5) −0·017, C(13) 2·456, N(3) −1·964, Mo 0·228]

Plane (2):

N(1), N(2), C(3)—(5) $12{\cdot}663x - 6{\cdot}784y - 0{\cdot}436z = 1{\cdot}503$

[N(1) 0·001, N(2) 0·000, C(3) −0·001, C(4) 0·001, C(5) 0·000, Mo −0·193, B −0·098]

Plane (3):

N(3), N(4), C(6)—(8) $13{\cdot}087x + 7{\cdot}108y - 3{\cdot}432z = 3{\cdot}202$

[N(3) 0·001, N(4) −0·001, C(6) −0·000, C(7) −0·001, C(8) 0·001, Mo 0·010, B −0·078]

Plane (4):

N(5), N(6), C(9)—(11) $-1{\cdot}348x + 11{\cdot}678y - 3{\cdot}287z = 0{\cdot}504$

[N(5) −0·005, N(6) 0·001, C(9) 0·006, C(10) −0·005, C(11) 0·002, Mo −0·039, B 0·176]

The molybdenum–carbon distances to the 2-methylallyl group are 2·337(5), 2·258(4), and 2·364(4) Å, as compared with 2·358(9), 2·214(8), and 2·331(8) Å in the allylbis(1-pyrazolyl) compound. The allyl structure thus has the central carbon atom of the allyl system closer to the molybdenum atom by 0·117—0·144 Å so the substitution of a methyl group for a proton on the 2-position of the allyl group does not drastically alter the geometry. (In the methyl-substituted compound the central atom of the allyl group is 0·079—0·106 Å closer to the molybdenum atom than the end atoms.)

The distance between the molybdenum and boron atoms is 3·391(4) Å, significantly greater than the corresponding distances of 2·81 and 2·829(7) Å in the dihydrobispyrazolyl structures,[6,7] in which a proton on boron interacts with the molybdenum. In the structure of (benzenediazo)dicarbonyl[hydrotris(1-pyrazolyl)-borato]molybdenum,[13] where there is no proton involvement, this distance is 3·345(7) Å.

The line through the molybdenum and boron atoms forms an approximate three-fold axis for the pyrazolyl rings. However, although the rings are planar (maximum standard deviation 0·006 Å), they are slightly skewed from the three-fold symmetry, for neither the

---

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1970, Index issue. (Items less than 10 pp. are sent as full size copies.)

[13] G Avitabile, P. Ganis, and M. Nemiroff, *Acta Cryst.*, 1971, **B27**, 725.

molybdenum nor the boron atoms lie on the planes of any of the rings. In fact they lie on opposite sides of the planes of two of the rings (Table 4). This skewing of the rings in the terdentate pyrazolylborate ligand differs from that seen in bis[hydrotris(1-pyrazolyl)borato]-cobalt[14] where the pyrazolylborate rings are distorted from D_{3d} symmetry by slight rotations of the pyrazolyl rings about their N–N axes and in which the bonded cobalt and boron atoms thus lie on the same sides of the planes of the rings.

Examination of the non-bonded contact distances for nitrogen and carbon atoms of the pyrazolyl rings supports the suggested explanation of the n.m.r. data. In the crystal structure the plane of the ring N(3), N(4), C(6)—(8) is situated between the carbonyl groups and has many close contact distances; *e.g.* N(3) ··· C(1) 2·868(6), N(3) ··· C(2) 2·932(4), C(6) ··· C(1) 3·249(6), and C(6) ··· C(2) 3·391(4) Å. The other two rings are each somewhat further from one carbonyl group and are greatly removed from the other. Thus in circumstances where rotation about the Mo–B axis is restricted to the point where the molecules have the same geometry as those in single crystals, the protons on the N(3), N(4), C(6)—(8)-ring might be expected to show the effects of an environment which differs markedly from those of the other two, which are fairly similar.

We thank the Danish National Research Council for Natural Sciences for a grant towards the cost of the *X*-ray diffractometer, and the North Atlantic Treaty Organization for a grant to support this work. Computations performed using the XDS Sigma 7 were made at the University of Wyoming, and those on the IBM 360/75 at the Northern Europe University Computing Center, Lyngby, Denmark. K. J. W. thanks Professor C. G. Ballhausen for his continued support.

[3/435 *Received*, 26*th February*, 1973]

---

[14] M. R. Churchill, K. Gold, and C. E. Maw, jun., *Inorg. Chem.*, 1970, **9**, 1597.