

Crystal Structure of Dicarbonyl(π -cyclopentadienyl)[di-(*t*-butyl)methyleneamino]molybdenum(II)

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Crystals of the title compound are monoclinic, space group $P2_1/n$, with $a = 12.674(1)$, $b = 8.279(1)$, $c = 16.543(2)$ Å, $\beta = 100.82(3)^\circ$, $Z = 4$. The structure was solved from diffractometer data by the heavy-atom method and refined by least squares to R 0.033 for 1543 observed reflections. The $\text{Bu}_2\text{C}:\text{N}$ group is attached to Mo by a short bond of length 1.892 Å, the Mo-N-C angle being 171.8° . Both these values are consistent with the existence of substantial Mo-N multiple bonding.

THE title compound, $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{N}:\text{C}\text{Bu}_2^t)$, was prepared¹ by the reaction between tricarbonylchloro-(π -cyclopentadienyl)molybdenum and di-(*t*-butyl)methyleneaminolithium. Changes with temperature were found in both the i.r. and ¹H n.m.r. solution spectra of the complex and these were interpreted in terms of conformational changes arising through rotation about the multiple metal-nitrogen bond. The present study was undertaken to provide information about the mode of bonding of the methyleneamino-group to the transition-metal atom and about the molecular conformation in the solid state.

EXPERIMENTAL

Crystals of the complex were obtained directly from the reaction mixture as hexagonal plates, elongated along b ,

with well developed {001} faces. The crystal used for data collection had dimensions: $0.4 \times 0.7 \times 0.3$ mm.

Crystal Data.— $\text{C}_{16}\text{H}_{23}\text{MoNO}_2$, $M = 357.29$, Monoclinic, $a = 12.674(1)$, $b = 8.279(1)$, $c = 16.543(2)$ Å, $\beta = 100.82(3)^\circ$, $U = 1705$ Å³, $D_m = 1.38$, $Z = 4$, $D_c = 1.39$ g cm⁻³, $\mu = 7.5$ cm⁻¹ for Mo- K_α radiation, $\lambda = 0.7107$ Å. Space group $P2_1/n$.

X-Ray intensities were measured on a Hilger and Watts Y 290 four-circle diffractometer by use of Zr-filtered Mo-radiation and employing a θ - 2θ scan. 1543 Reflections having net counts $>3\sigma$ were obtained within the range $0 < \theta \leq 22.5^\circ$. Intensities were corrected for Lorentz and polarisation factors but not for absorption. Unit-cell parameters were obtained by a least-squares treatment² of the positions of 12 high-order reflections.

Structure Determination and Refinement.—The position

¹ M. Kilner and C. Midcalf, *J. Chem. Soc. (A)*, 1971, 292.

² W. R. Busing and H. A. Levy, *Acta Cryst.*, 1967, **22**, 457.

of the molybdenum atom was found from the Patterson function and those of the other non-hydrogen atoms by Fourier methods. Atomic parameters were refined by the method of least squares, by use of the block-diagonal approximation and, with anisotropic temperature factors for all these atoms, R was 0.041. Two difference-Fourier syntheses then revealed the positions of all 23 hydrogen atoms. The hydrogen atoms in the cyclopentadienyl group were placed at calculated positions, which were in good agreement with those obtained from the difference-Fourier map, but the remaining hydrogen atoms were

TABLE 1

Final positional (fractional) and thermal parameters* for non-hydrogen atoms, with standard deviations in parentheses

	x	y	z
Mo	-0.04214(4)	0.04705(7)	0.20340(3)
O(1)	-0.0909(5)	0.3942(7)	0.1362(3)
O(2)	0.0929(4)	0.0867(6)	0.0660(3)
N	0.0651(4)	0.1070(6)	0.2941(3)
C(1)	-0.0917(9)	-0.2066(16)	0.2502(11)
C(2)	-0.1665(10)	-0.0919(15)	0.2670(6)
C(3)	-0.2207(6)	-0.0335(10)	0.1935(7)
C(4)	-0.1837(7)	-0.1102(12)	0.1322(5)
C(5)	-0.1055(9)	-0.2091(11)	0.1645(9)
C(6)	-0.0740(6)	0.2662(9)	0.1615(4)
C(7)	0.0452(5)	0.0704(8)	0.1176(4)
C(8)	0.1284(5)	0.1367(8)	0.3607(4)
C(9)	0.2345(5)	0.0381(9)	0.3796(4)
C(10)	0.2486(6)	-0.0575(11)	0.3036(5)
C(11)	0.3321(6)	0.1471(11)	0.4039(5)
C(12)	0.2303(6)	-0.0802(9)	0.4473(5)
C(13)	0.0937(5)	0.2674(8)	0.4165(4)
C(14)	0.1381(10)	0.2467(14)	0.5051(5)
C(15)	-0.0235(7)	0.2643(14)	0.4108(6)
C(16)	0.1232(12)	0.4306(10)	0.3872(7)

	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
Mo	54(1)	119(1)	36(1)	-9(1)	8(1)	-12(1)
O(1)	136(6)	148(10)	83(3)	49(10)	-18(7)	16(12)
O(2)	124(5)	326(15)	52(3)	-42(10)	83(6)	-120(13)
N	55(4)	121(9)	35(2)	-7(8)	28(6)	24(9)
C(1)	97(10)	288(27)	164(11)	320(32)	-54(18)	-121(25)
C(2)	160(11)	385(30)	46(4)	-16(19)	58(13)	-348(29)
C(3)	53(6)	208(16)	98(6)	-34(19)	47(11)	-37(17)
C(4)	84(8)	253(20)	63(5)	-76(16)	8(10)	-140(20)
C(5)	101(10)	99(15)	171(10)	-47(22)	119(18)	-55(19)
C(6)	78(6)	167(14)	44(3)	-17(13)	-1(7)	-24(17)
C(7)	78(6)	134(14)	44(3)	-24(11)	-6(7)	-27(14)
C(8)	52(5)	122(11)	33(3)	1(10)	18(7)	-6(13)
C(9)	59(5)	193(13)	35(3)	37(13)	14(6)	59(16)
C(10)	112(8)	436(25)	59(4)	-60(17)	18(9)	283(24)
C(11)	56(6)	308(19)	97(5)	37(18)	19(9)	-6(19)
C(12)	110(8)	212(18)	74(5)	92(14)	37(10)	117(18)
C(13)	60(5)	168(13)	31(3)	-22(10)	19(6)	24(13)
C(14)	356(19)	549(32)	41(4)	-122(19)	-21(14)	587(42)
C(15)	118(10)	622(36)	147(8)	-406(29)	142(15)	-70(29)
C(16)	403(20)	171(19)	127(7)	-40(20)	324(21)	55(31)

* Anisotropic temperature factors are in the form:

$$\exp[-10^{-4}(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$$

placed at their observed sites. All hydrogen atoms were included in the structure-factor calculations, with isotropic temperature factors based on those of the carbon atoms to which they were attached, but their parameters were not

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-size copies.)

³ G. H. Stout and L. H. Jensen, 'X-Ray Structure Determination,' Macmillan, London, 1969.

refined. Further refinement, employing full-matrix least-squares methods, saw R converge to its final value of 0.033 for the 1543 observed reflections. A difference-Fourier map calculated at the end of the refinement showed no peaks with heights $>0.4 \text{ e}\text{\AA}^{-3}$.

In the final cycle of refinement, the parameter shifts were all $<0.25\sigma$, and the weighting was given³ by: $\sqrt{w} = 2N/|F_o| \cdot \{T + g \cdot B + (0.05 \cdot N)^2\}^{\frac{1}{2}}$ where N is the net

TABLE 2

Positional (fractional) and thermal parameters for the hydrogen atoms

	x	y	z	$B/\text{\AA}^2$
H(1)	-0.035	-0.273	0.296	8.9
H(2)	-0.176	-0.054	0.330	8.2
H(3)	-0.285	0.059	0.185	6.7
H(4)	-0.215	-0.086	0.066	7.0
H(5)	-0.059	-0.287	0.131	9.0
H(6)	0.310	-0.133	0.317	8.1
H(7)	0.175	-0.150	0.292	8.1
H(8)	0.260	0.033	0.267	8.1
H(9)	0.400	0.083	0.408	7.8
H(10)	0.330	0.217	0.458	7.8
H(11)	0.330	0.233	0.358	7.8
H(12)	0.290	-0.150	0.467	7.3
H(13)	0.155	-0.150	0.442	7.3
H(14)	0.250	0.000	0.500	7.3
H(15)	0.180	0.350	0.500	11.1
H(16)	0.080	0.283	0.533	11.1
H(17)	0.180	0.167	0.558	11.1
H(18)	-0.060	0.233	0.350	10.6
H(19)	-0.070	0.383	0.417	10.6
H(20)	-0.060	0.183	0.442	10.6
H(21)	0.040	0.450	0.350	11.6
H(22)	0.180	0.433	0.350	11.6
H(23)	0.150	0.483	0.450	11.6

count and g is the ratio of the time spent measuring the total count (T) to that spent measuring the two backgrounds, whose sum is B . Unobserved reflections were given zero weight in the refinement. Scattering factors were taken from ref. 4, hydrogen form factors from ref. 5. The real and imaginary parts of the dispersion correction were applied in the case of molybdenum. The atomic parameters of the non-hydrogen atoms are shown in Table 1 and those of the hydrogen atoms in Table 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20845 (4 pp.).*

RESULTS AND DISCUSSION

The co-ordination about the molybdenum atom can be regarded as based on a distorted octahedron if the cyclopentadienyl ligand is considered to occupy three co-ordination sites. The other three sites are then occupied by the methyleneamino-ligand and the two carbonyl groups, which are mutually *cis* (Figure 1).

The Mo-N distance of 1.892(5) Å (Table 3) is much shorter than the lengths generally observed for single bonds. In *cis*-Mo(dien)(CO)₂ [dien = NH(CH₂CH₂NH₂)₂]⁶ the mean Mo-N bond length is 2.32 Å and the

⁴ 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

⁵ R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1966, **42**, 3175.

⁶ F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 314.

same distance was found in $\text{MoO}_3(\text{dien})^7$ and $\text{MoO}_2(\text{C}_9\text{H}_6\text{NO})_2$.⁸ However, a smaller value has been re-

TABLE 3

(a) Bond lengths (Å) and their standard deviations

Mo-N	1.892(5)	C(8)-C(9)	1.55(1)
		C(8)-C(13)	1.54(1)
Mo-C(6)	1.957(8)		
Mo-C(7)	1.966(7)	C(9)-C(10)	1.52(1)
		C(9)-C(11)	1.52(1)
C(1)-C(2)	1.41(2)	C(9)-C(12)	1.50(1)
C(2)-C(3)	1.37(2)	C(13)-C(14)	1.48(1)
C(3)-C(4)	1.35(1)	C(13)-C(15)	1.47(1)
C(4)-C(5)	1.32(1)	C(13)-C(16)	1.51(1)
C(1)-C(5)	1.40(2)		
		Mo-C(1)	2.36(1)
C(6)-O(1)	1.14(1)	Mo-C(2)	2.35(1)
C(7)-O(2)	1.14(1)	Mo-C(3)	2.34(1)
		Mo-C(4)	2.35(1)
N-C(8)	1.26(1)	Mo-C(5)	2.32(1)

(b) Bond angles (deg.) and their standard deviations

Mo-N-C(8)	171.8(4)	N-C(8)-C(9)	117.3(5)
		N-C(8)-C(13)	117.1(5)
Mo-C(6)-O(1)	178.6(6)	C(9)-C(8)-C(13)	125.6(5)
Mo-C(7)-O(2)	177.5(6)		
		C(8)-C(9)-C(10)	109.7(5)
C(1)-C(2)-C(3)	108.0(11)	C(8)-C(9)-C(11)	111.8(5)
C(2)-C(3)-C(4)	108.3(9)	C(8)-C(9)-C(12)	110.1(5)
C(3)-C(4)-C(5)	109.1(9)	C(10)-C(9)-C(11)	108.1(6)
C(4)-C(5)-C(1)	110.1(11)	C(10)-C(9)-C(12)	107.7(6)
C(5)-C(1)-C(2)	104.4(12)	C(11)-C(9)-C(12)	109.3(6)
		C(8)-C(13)-C(14)	114.5(6)
C(6)-Mo-C(7)	76.1(3)	C(8)-C(13)-C(15)	110.3(6)
C(6)-Mo-N	96.2(3)	C(8)-C(13)-C(16)	108.8(6)
C(7)-Mo-N	97.4(3)	C(14)-C(13)-C(15)	104.7(7)
		C(14)-C(13)-C(16)	110.6(7)
		C(15)-C(13)-C(16)	107.7(7)

(c) Some intramolecular non-bonding contacts (Å)

Mo...C(10)	3.84	C(7)...C(10)	3.78
Mo...C(15)	3.84	C(11)...C(13)	3.22
O(1)...O(2)	3.78	C(11)...C(14)	3.33
O(1)...N	3.80	C(11)...C(16)	3.51
O(1)...C(7)	3.23	C(12)...C(13)	3.35
O(2)...N	3.86	C(12)...C(14)	3.17
O(2)...C(6)	3.23		

(d) Intermolecular distances (Å) < 4 Å for non-hydrogen atoms

O(1)...C(1 ^I)	3.81	O(2)...C(11 ^{VIII})	3.77
O(1)...C(2 ^V)	3.73	O(2)...C(12 ^{IV})	3.59
O(1)...C(5 ^I)	3.33	O(2)...C(16 ^{VII})	3.76
O(1)...C(11 ^{VIII})	3.80	C(1)...C(3 ^{VI})	3.83
O(1)...C(12 ^{VIII})	3.82	C(2)...C(6 ^{VI})	3.88
O(1)...C(14 ^{VIII})	3.88	C(2)...C(14 ^{III})	3.94
O(2)...O(2 ^{II})	3.23	C(3)...C(15 ^{VI})	3.77
O(2)...C(4 ^{II})	3.68	C(4)...C(12 ^{IX})	3.98
O(2)...C(5 ^{II})	3.98	C(4)...C(15 ^{VI})	3.79
O(2)...C(7 ^{II})	3.46	C(7)...C(11 ^{VIII})	3.88
O(2)...C(10 ^{VI})	3.97	C(10)...C(16 ^{VII})	3.81

Superscripts in Roman refer to the following equivalent positions, with respect to the reference molecule at x, y, z :

I $x, 1+y, z$	VI $-\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$
II $-x, -y, -z$	VII $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$
III $-x, -y, 1-z$	VIII $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
IV $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$	IX $-\frac{1}{2}+x, -\frac{1}{2}-y, -\frac{1}{2}+z$
V $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$	

ported in $(\text{C}_5\text{H}_5)_3\text{MoNO}$, where the Mo-N distance of 1.75 Å has been interpreted⁹ in terms of considerable

⁷ F. A. Cotton and R. C. Elder, *Inorg. Chem.*, 1964, **3**, 397.

⁸ L. O. Atovmyan and Yu. A. Sokolova, *Chem. Comm.*, 1969, 649.

⁹ F. A. Cotton, J. C. Calderon, and P. Legzdins, *J. Amer. Chem. Soc.*, 1969, **91**, 2528.

$d_{\pi-p_{\pi}}$ back-bonding. In the present case, the Mo-N-C(8) angle of 171.8° agrees with the earlier conclusion¹⁰ that the nitrogen atom is formally in an sp hybrid state. The filled p orbital on the nitrogen can overlap with an empty d orbital on the molybdenum atom and in addition back-donation can take place from a filled metal d orbital into the empty π^* -orbital of the ligand, substantially increasing the Mo-N bond-order. The cylindrical symmetry of the d -orbitals involved in the $d_{\pi-p_{\pi}}$ bonding will also allow rotation about the Mo-N bond in the same way as that suggested for the carbene group.¹¹

The Mo-C(6) and Mo-C(7) distances of 1.957 and 1.966 Å do not differ significantly from one another and

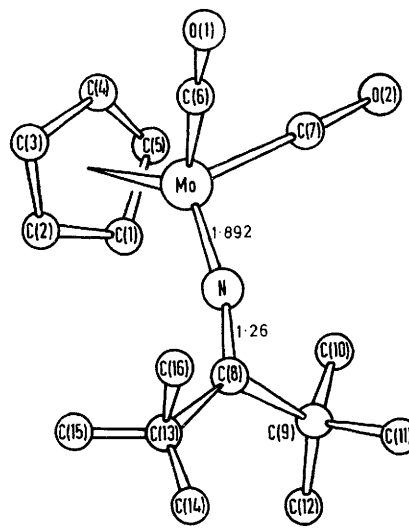


FIGURE 1 A view of the molecule, showing the atom numbering

are very similar to the mean lengths of 1.975 in $(\pi\text{-C}_5\text{H}_5)_3\text{Mo}(\text{CO})_3\text{Et}$ ¹² and 1.943 Å in $(\pi\text{-C}_5\text{H}_5)_3\text{MoNCS}(\text{CO})_2(\text{C}_{10}\text{H}_8\text{N}_2)$.¹³ The two C-O distances are 1.14 Å, compared with 1.16 and 1.17 Å in the afore-mentioned compounds, and as expected the Mo-C-O units are almost linear, the mean angle being 178.1°. The distribution of the ligands around the molybdenum atom is such that both the C(6)-Mo-N and C(7)-Mo-N angles are close to 97°, while the C(6)-Mo-C(7) angle is just over 76°. The two carbonyl groups are thus compressed towards each other while being pushed away from the t-butyl groups, reflecting the bulky nature of the latter.

In the cyclopentadienyl ligand, the C-C distances lie in the range 1.32—1.41 Å. Considerable variations in these bond lengths have been reported and in $(\pi\text{-C}_5\text{H}_5)_3\text{Mo}(\text{CO})_2(\text{CH}_2\text{-C}_6\text{H}_4\text{Me})$ the range 1.35—1.42 Å was

¹⁰ M. Kilner and C. Midcalf, *Chem. Comm.*, 1970, 552.

¹¹ O. S. Mills and A. D. Redhouse, *Angew. Chem. Internat. Edn.*, 1965, **4**, 1082.

¹² M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 1963, 273.

¹³ A. J. Graham and R. H. Fenn, *J. Organometallic Chem.*, 1969, **17**, 405.

attributed¹⁴ to librational or rotational disorder. The five carbon atoms are coplanar (Table 4).

In the methyleamino-group, the N-C(8) bond length [1.259(8) Å] falls within the range of values found for

TABLE 4

Equations of some weighted least-squares mean planes (X , Y , Z in Å with respect to orthogonal axes a , b , c^*) and their deviations, Δ (Å), from the planes

$$-0.6892X - 0.7244Y - 0.0160Z - 2.5016 = 0$$

	C(1)	C(2)	C(3)	C(4)	C(5)	Mo *
Δ	0.009	0.006	-0.010	0.012	-0.017	-2.033
σ	0.012	0.013	0.008	0.010	0.010	0.001

$$0.5509X + 0.6964Y - 0.4600Z + 1.6293 = 0$$

	N	C(8)	C(9)	C(13)	Mo *
Δ	-0.001	0.001	-0.001	-0.001	-0.262
σ	0.005	0.006	0.007	0.006	0.001

* Atoms not included in the mean plane calculations.

carbon-nitrogen double-bonds, e.g. 1.276 in formaldoxime,¹⁵ 1.288 in formamidoxime,¹⁶ and 1.26 Å in *syn*- and *anti-p*-chlorobenzaldoxime.¹⁷ The value is also close to those of 1.26 and 1.27 Å in $\text{Li}(\text{AlN}:\text{C}\text{Bu}^t_2)_4$ ¹⁸ for terminal and bridging methyleamino-groups and to that (1.28 Å) in $(\text{Ph}_2\text{AlN}:\text{CPh}\cdot\text{C}_6\text{H}_4\text{Br})_2$ ¹⁹ for a bridging unit. The lengths of the bonds C(8)-C(9) and C(8)-C(13) do not differ significantly from one another and their mean (1.546 Å) is greater than the value expected for a $\text{C}(sp^3)\text{-C}(sp^2)$ bond²⁰ though a mean of 1.56 Å was found in $\text{LiAl}(\text{N}:\text{C}\text{Bu}^t_2)_4$.¹⁸ The six C-C distances within the two *t*-butyl groups range from 1.47 to 1.52 Å, mean 1.50 Å. The C-H distances within the two *t*-butyl groups range from 0.96 to 1.19 Å, mean 1.06 Å.

The bulkiness of the *t*-butyl groups may be illustrated by considering the mean plane through the atoms N, C(8), C(9), and C(13). The orientation of this plane (Table 4) is such that the two carbonyl groups lie on one side with the cyclopentadienyl group on the other. The plane makes an angle of 50° with the mean plane through the atoms Mo, N, O(1), C(6), C(8) and an angle of 125° with the plane of Mo, N, O(2), C(7), C(8), whilst

¹⁴ F. A. Cotton and M. D. LaPrade, *J. Amer. Chem. Soc.*, 1968, **90**, 5418.

¹⁵ I. N. Levine, *J. Chem. Phys.*, 1963, **38**, 2326.

¹⁶ D. Hall, *Acta Cryst.*, 1965, **18**, 955.

¹⁷ K. Falting, W. N. Lipscomb, and P. Jersley, *Acta Cryst.*, 1964, **17**, 1263.

¹⁸ K. Wade, H. M. M. Shearer, R. Snaith, and J. D. Sowerby, *Chem. Comm.*, 1971, 1275.

it is inclined at 88° to the plane based on the centroid of the cyclopentadienyl group, Mo, N, and C(8). As a result, the only close approach between any of the carbon atoms in a *t*-butyl group and atoms in the carbonyl groups is between C(7) and C(10). On the other hand there are no contacts <4 Å between carbon atoms in the cyclopentadienyl ring and in the *t*-butyl groups.

The packing of the molecules is shown in Figure 2, where the structure is viewed in projecting along the

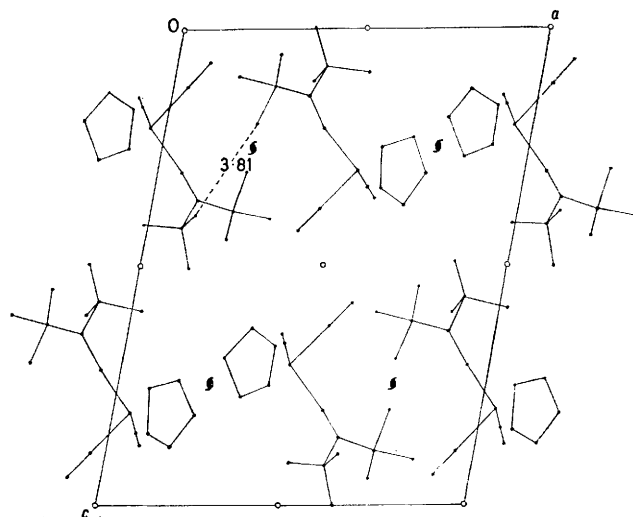


FIGURE 2 Packing of the molecules, in the projection along b

b axis. The only intermolecular contact less than 4 Å involving two methyl carbon atoms is $\text{C}(10) \cdots \text{C}(16^{\text{VII}})$ 3.81 Å. This contact would be decreased if the Mo-N-C(8) angle became 180° and may be responsible for the 8° deviation of this angle from linearity.

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[2/2896 Received, 28th December, 1972]

¹⁹ W. S. McDonald, *Acta Cryst.*, 1969, **B25**, 1385.

²⁰ M. J. S. Dewar and H. N. Schmeising, *Tetrahedron Letters*, 1959, **5**, 166.

²¹ F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Huber, N.R.C. Crystallographic Programs for the IBM 360 System, World List of Crystallographic Computer Programs, 2nd edn., Appendix p. 52.