ON INTERNAL ROTATION IN GASEOUS BENZENECHROMIUM TRICARBONYL

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Summary

The vapor phase molecular structure of benzenechromium tricarbonyl, $C_6H_6Cr(CO)_3$, has been studied by electron diffraction. On the basis of the diffraction data and of auxiliary vibrational calculations, it is concluded that in the vapor phase the molecule is a nearly unhindered internal rotor. Its vapors consist of a mixture of several conformations which differ by the rotational arrangement of the six-ring with respect to the carbonyl groups, whereas solid state studies showed the molecule to be in the pure staggered form. The C—C bond distance of the six-ring (r_a) was found to be 1.417 ± 0.003 Å and slightly longer than in free benzene (1.397 Å). The OC—Cr—CO bond angle was found to be $88.6 \pm 1.1°$ indicating a semi-octahedral arrangement; $r_a(Cr—C(CO)) = 1.863 \pm 0.005$ Å and $r_a(Cr—C(C_6H_6)) = 2.208 \pm 0.006$ Å.

Introduction

Benzenechromium tricarbonyl, $C_6H_6Cr(CO)_3$ (BCT, henceforth), is the interesting prototype of an important class of transition metal complexes. In the recent past this molecule has therefore been the object of several structural studies involving infrared [1-3], Raman [3,4], X-ray diffraction [5-7] and Neutron diffraction techniques [7]. The previous investigations [1-7] have in common that they were all concerned with the solid state, and no vapor phase study of the molecule has been reported yet.

Solid state studies have in general the disadvantage of examining molecules in a frozen state. This means that the dynamical features of structure which a molecule might display can remain unobserved. In the case of BCT, e.g., such aspects of molecular dynamics are of importance with respect to the relative orien-
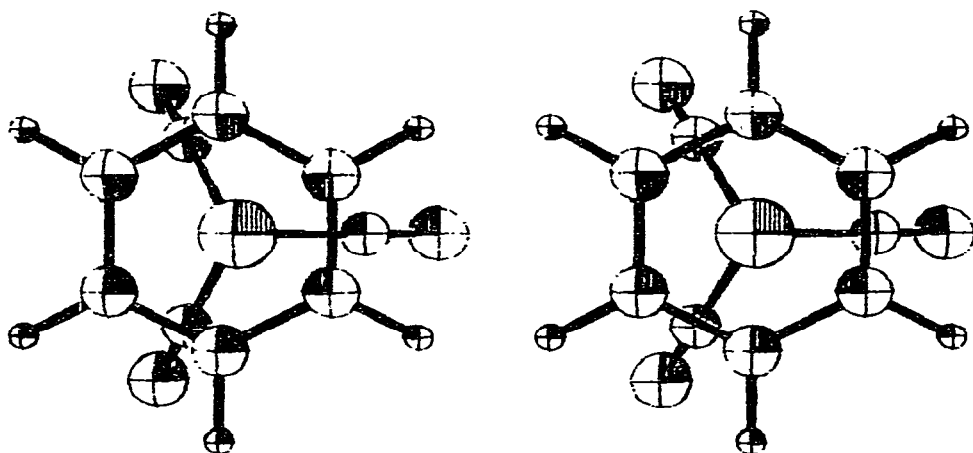
Fig. 1. Stereoscopic presentation of the staggered form (BCT(1)) of BCT (top view).

tation of the six-membered ring and the carbonyl groups. In principle, the three carbonyl ligands in BCT can be expected to be found in a staggered [BCT(1), (Figs. 1 and 2)] or in an eclipsed [BCT(2), (Fig. 3)] arrangement with respect to the carbon atoms of the benzene ring. Conformation BCT(1) was found for BCT in the solid state [6,7]. Conformations BCT(1) or BCT(2) are usually found for substituted benzenechromium tricarbonyls [8,9] in the solid state, depending on the electron-withdrawing or electron-donating nature of the substituents.

It is an interesting question whether in the vapor phase the benzene ring of BCT is also arranged in the staggered conformation or in some other way; e.g., eclipsed or in various stages of an internal rotational mode. (See e.g. model BCT(1,2,3), Fig. 4.) Such a difference in the conformational composition of crystalline and gaseous BCT would be possible if the energy differences between different rotational states were so small that the crystal structure could be deter-
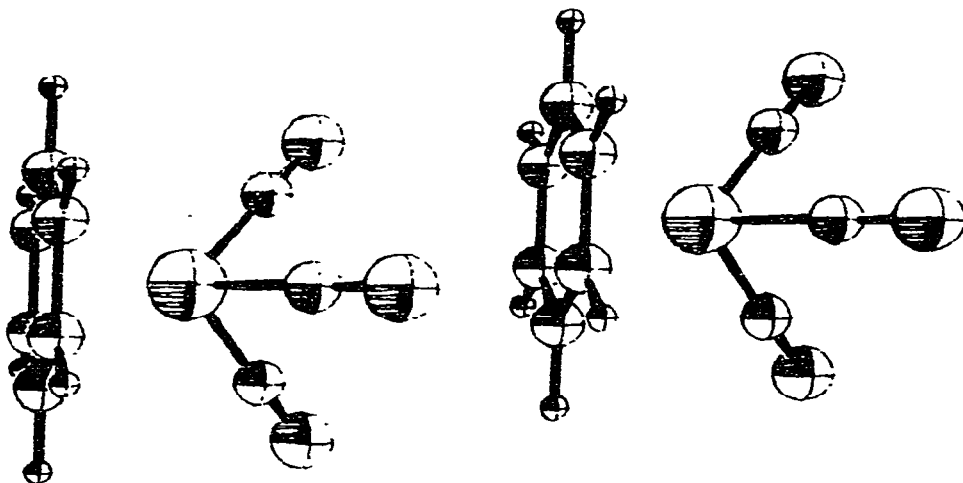

Fig. 2. Stereoscopic presentation of the staggered form (BCT(1)) of BCT (side view).
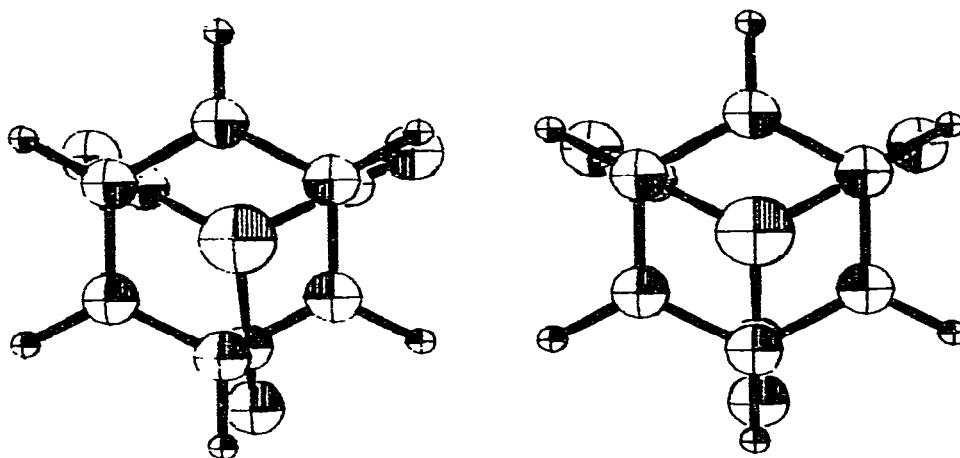
Fig. 3. Stereoscopic presentation of the eclipsed form (BCT(2)) of BCT.

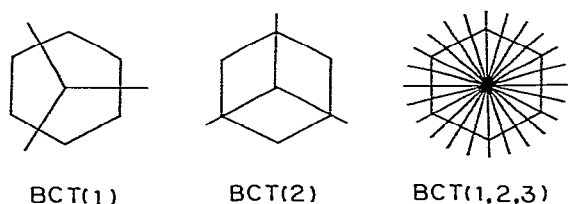BCT(1)   BCT(2)   BCT(1,2,3)

Fig. 4. Schematic of molecular models (BCT(1), BCT(2) and BCT(1,2,3)) of BCT. For more explanations see text.

mined by packing forces rather than by the intramolecular potential. The purpose of the present study was to investigate this matter, and we chose vapor phase electron diffraction as the appropriate tool. Since the same factors which favor the display of dynamical structural features also lead to a loss of orientational specificity and often make it difficult to interpret diffraction patterns in a conclusive way, we have also complemented this diffraction data analysis of BCT by vibrational calculations of the molecule.

Experimental (electron diffraction)

A commercial sample of benzenechromium tricarbonyl (Strem Chemical Co.) was sublimed, and its identity confirmed spectroscopically.

Electron diffraction pictures of BCT vapors were recorded at the University of Oslo (Balzer's Eldigraph KD-62) at a nozzle temperature of 140°C .Two sets of five plates each were taken at two different nozzle to plate distances (25 and 58 cm) corresponding to s-ranges of 4.0-29.25 $Å^{-1}$ and of 1.0-12.75 $Å^{-1}$, respectively.

Individual curves were reduced in the usual way [10]. Scattering factors were those used by Yates, Bonham and Schäfer [11]. Empirical backgrounds were obtained by a least squares procedure [12], one each for each plate and each BCT model in a consistent manner. Some of the reduced curves of data, selected at random, are shown in Fig. 5 with the final backgrounds for the best
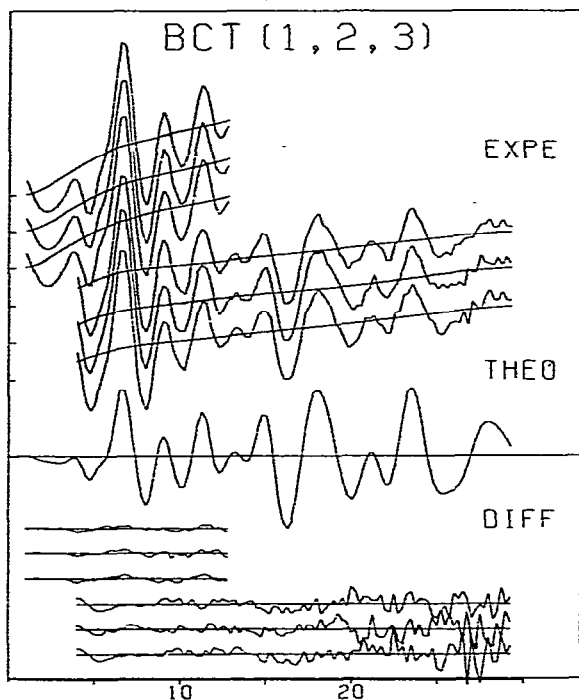
Fig. 5. Experimental intensities (from the data reduction process) plus their empirical backgrounds (values for BCT(1,2,3)); theoretical intensities for the refined model of BCT(1,2,3); and the corresponding differences theory-experiment. Upper curves range from $s = 1.0$ to $s = 12.75$ Å^{-1}; lower curves from $s = 4.0$ to $s = 29.25$ Å^{-1}.

fitting model (BCT(1,2,3), explanations below). All curves are available on request *.

Experimental RD-curves shown in the Figs. 6 and 7 were obtained from average experimental curves (connections of individual plates) after adding theoretical intensity points from $s = 0.0$ to $s = 1.0$ Å^{-1}.

Vibrational calculations

Mean amplitudes of vibration are available from a previous investigation for benzenechromium tricarbonyl in the conformation of BCT(1) [13]. These values were obtained from a vibrational analysis based on symmetry coordinates [14] and a force field refined from the vibrational spectra [4]. We have now performed additional vibrational calculations in order to determine the extent to which the calculated mean amplitudes depend on the rotational state of the six-ring. These calculations were carried out using cartesian coordinates as a basis for vibrational analysis. The use of these coordinates has the advantage that different conformations can be treated without geometrical difficulties, but the disadvantage that no BCT force constants are known for them. It was therefore necessary to make approximations as follows.

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* Data curves from individual plates as well as experimental backgrounds for individual theoretical models will be mailed on request by the authors. Complete listings of data were also published in ref. 32.
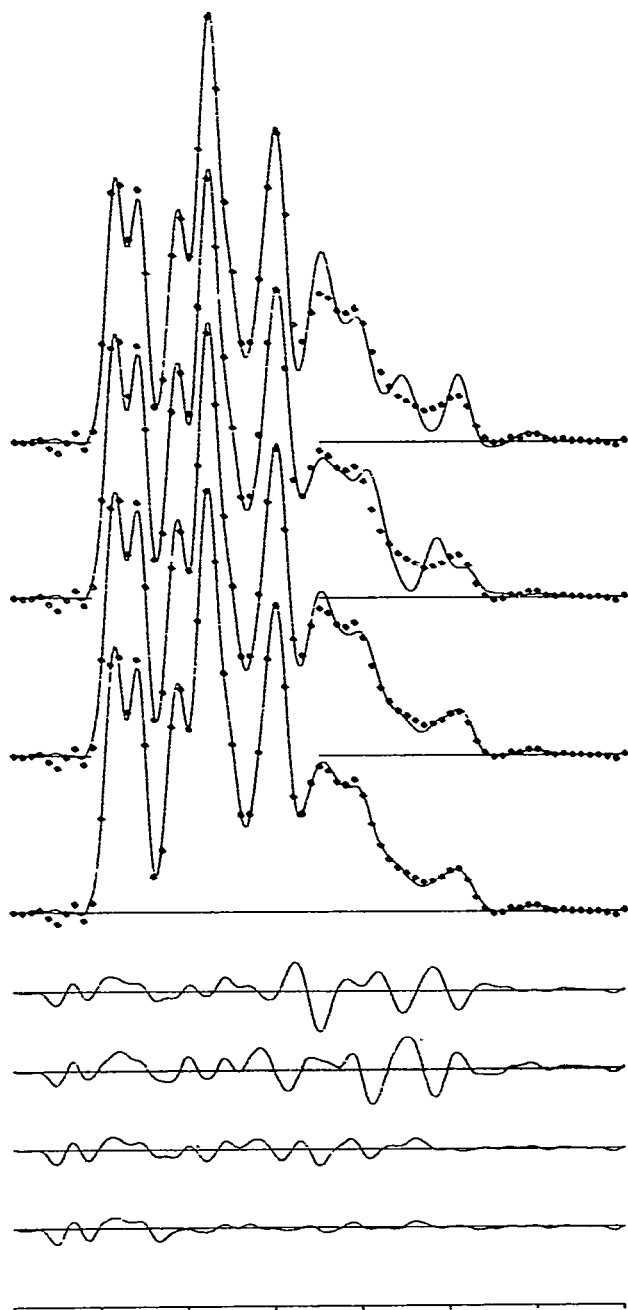
Fig. 6. Experimental (dotted lines) and theoretical radial distribution curves for BCT from $r = 0.0$ to $r = 7.0$ Å. The first curve (from top) is for BCT(1); the second for BCT(2); the third is for BCT(1,2); all with spectroscopic mean amplitudes (see Table 1). The fourth curve is for BCT(1,2) with mean amplitudes and concentrations refined by least squares from the diffraction data. The following curves give the corresponding differences theory-experiment. The used damping factor was $k = 0.0036$ Å^2.
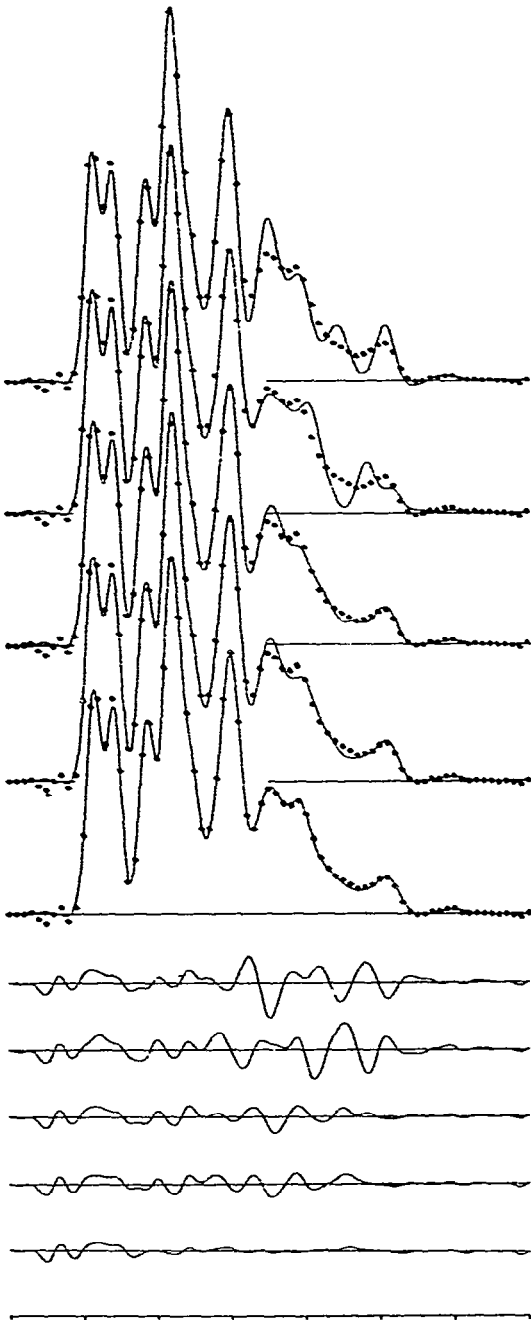
Fig. 7. Experimental (dotted lines) and theoretical (solid lines) radial distribution curves as in Fig. 6. First curve (from top) is for BCT(1); second curve for BCT(2); third curve for BCT(3) and fourth curve for BCT(1,2,3); all with spectroscopic mean amplitudes (see Table 1). The last curve is for BCT(1,2,3) with mean amplitudes and concentrations refined from the diffraction data. The following curves give the corresponding difference theory-experiment.

Valence force constants were chosen by analogy to complexed benzene [15] and $Cr(CO)_6$ [16] in such a way that the calculations reproduced approximately the refined mean amplitudes calculated before [13] for BCT(1). This approximate force field was then used without any change in vibrational analyses based on the different cartesian coordinate sets of all the five conformations of BCT (BCT(1) to BCT(5)) described below. By employing Gwinn's vibrational program [17] together with the amplitude program of Stølevik, Seip and Cyvin [18] this procedure gave the calculated mean amplitudes listed in Table 1.

This selection of force constants is somewhat arbitrary and very approximate, and this is a deficiency of our vibrational calculations. It does not, however, affect the conclusions below even where mean amplitudes are used in further calculations. This is so because our field is seen (Table 1) to produce mean amplitudes for BCT(1) with deviations from the more accurately refined ones, which have no significant effect on the electron diffraction data analysis. These calculations should therefore give estimates of mean amplitude shifts within the right order of magnitude.

It is interesting to note how much the mean amplitudes of a molecule can change when only its coordinates change and the force field remains constant. The effect is caused mainly by frequency shifts produced by the changing geometry of the molecule. These results are therefore in agreement with a series of similar studies which show that the vibrational properties of a molecule can change considerably due to a variety of factors not related to its force field. In addition to structural changes, these factors can include complex formation and kinematic coupling [19-23] and interesting correlations with chemical reactivity have been noted in this context [24].

Data analysis

Five models of BCT were investigated in this study. The staggered and eclipsed forms have already been mentioned above (namely BCT(1) and BCT(2), Figs. 1-3).

Transformation from the eclipsed to the staggered conformation* corresponds to a rotation of the six-ring by 30° around the threefold symmetry axis of the molecule. Three models with rotational arrangements between the staggered and eclipsed conformations were investigated. In model three (BCT(3)) the benzene ring is rotated by 15° from the eclipsed or staggered arrangements; in model four (BCT(4)) and model five (BCT(5)) the ring is 7.5° from the eclipsed and the staggered positions, respectively.

In all the models described above the six-ring was assumed to be planar, having one C—C bond distance and one C—H bond distance only and six-fold local symmetry. The planarity or non-planarity of complexed benzene has been object of controversy for many years [25]. The planarity and six-fold symmetry of complexed benzene is now so well established [26] for Cr complexes in the vapor phase that any solution to the diffraction data involving a model with distorted C_6H_6 would be unacceptable.

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* In the following the term "conformation" is used for different forms of BCT which differ by the rotational arrangement of the six-ring with respect to the carbonyls. It is not implied that all these forms are different potential energy minima. They could also be part of one or several broad energy minima.

TABLE 1

MEAN AMPLITUDES OF VIBRATION (IN Å) FOR BCT

Values in column a for BCT(1) from ref. 13, column b, values for BCT(1), this study. All other values calculated as described in the text. Values from ref. 13 are for 0°C; values from this study are for 140°C, the temperature of the diffraction study.

Only values for distances between the benzene ring and the tricarbonyl group are reported, since the other mean amplitudes do not change significantly, when the conformation of the molecule changes.

Type	BCT(1) a			BCT(1) b			BCT(2)		
	(R_{ij})	u_{ij}	i,j	(R_{ij})	u_{ij}	i,j	(R_{ij})	u_{ij}	i,j
C—C	(3.479)	0.107	2,14	(3.501)	0.107	2,14	(3.190)	0.117	2,15
C—C							(3.786)	0.095	3,14
C—C	(3.960)	0.087	2,15	(3.983)	0.090	2,15	(4.052)	0.087	2,14
C—C									
C—C	(2.920)	0.103	2,16	(2.941)	0.119	2,16			
C—C							(2.845)	0.134	3,16
C—O	(5.084)	0.093	2,18	(5.101)	0.095	2,18	(5.190)	0.090	2,17
C—O									
C—O	(4.475)	0.131	2,17	(4.476)	0.124	2,17	(4.073)	0.140	2,18
C—O							(4.845)	0.104	3,17
C—O	(3.770)	0.136	2,19	(3.750)	0.146	2,19			
C—O							(3.624)	0.166	3,19
H—C	(4.049)	0.173	8,14	(4.062)	0.176	8,14	(4.493)	0.155	9,14
H—C							(3.580)	0.191	8,15
H—C	(4.774)	0.139	8,15	(4.784)	0.147	8,15	(4.886)	0.143	8,14
H—C									
H—C	(3.163)	0.180	8,16	(3.180)	0.204	8,16			
H—C							(3.021)	0.222	9,16
H—O	(4.931)	0.207	8,17	(4.928)	0.198	8,17	(4.263)	0.219	8,18
H—O							(5.513)	0.163	9,17
H—O	(5.891)	0.145	8,18	(5.905)	0.150	8,18	(6.043)	0.143	8,17
H—O									
H—O	(3.733)	0.223	8,19	(3.700)	0.241	8,19			
H—O							(3.472)	0.270	9,19

Type	BCT(3)			BCT(4)			BCT(5)		
	(R_{ij})	u_{ij}	i,j	(R_{ij})	u_{ij}	i,j	(R_{ij})	u_{ij}	i,j
C—C	(3.343)	0.106	2,15	(3.265)	0.109	2,15	(3.422)	0.106	2,15
C—C	(3.652)	0.102	3,14	(3.721)	0.098	3,14	(3.578)	0.104	3,14
C—C	(4.035)	0.088	2,14	(4.048)	0.087	2,14	(4.013)	0.089	2,14
C—C	(3.899)	0.093	3,15	(3.846)	0.093	3,15	(3.945)	0.092	3,15
C—C	(3.051)	0.121	2,16	(3.118)	0.121	2,16	(2.992)	0.119	2,16
C—C	(2.869)	0.120	3,16	(2.851)	0.128	3,16	(2.900)	0.117	3,16
C—O	(5.168)	0.091	2,17	(5.185)	0.090	2,17	(5.140)	0.093	2,17
C—O	(4.992)	0.099	3,18	(4.923)	0.100	3,18	(5.051)	0.097	3,18
C—O	(4.272)	0.124	2,18	(4.171)	0.129	2,18	(4.375)	0.124	2,18
C—O	(4.672)	0.117	3,17	(4.762)	0.111	3,17	(4.576)	0.121	3,17
C—O	(3.893)	0.148	2,19	(3.979)	0.148	2,19	(3.816)	0.148	2,19
C—O	(3.657)	0.148	3,19	(3.632)	0.159	3,19	(3.696)	0.145	3,19
H—C	(4.291)	0.165	9,14	(4.396)	0.159	9,14	(4.179)	0.171	9,14
H—C	(3.820)	0.179	8,15	(3.698)	0.182	8,15	(3.942)	0.178	8,15
H—C	(4.861)	0.143	8,14	(4.880)	0.143	8,14	(4.829)	0.144	8,14
H—C	(4.660)	0.152	9,15	(4.582)	0.154	9,15	(4.728)	0.150	9,15
H—C	(3.359)	0.202	8,16	(3.466)	0.199	8,16	(3.263)	0.202	8,16
H—C	(3.062)	0.208	9,16	(3.031)	0.216	9,16	(3.112)	0.204	9,16
H—O	(4.596)	0.201	8,18	(4.428)	0.205	8,18	(4.763)	0.200	8,18
H—O	(5.239)	0.181	9,17	(5.382)	0.171	9,17	(5.087)	0.190	9,17
H—O	(6.008)	0.143	8,17	(6.034)	0.142	8,17	(5.965)	0.146	8,17
H—O	(5.739)	0.158	9,18	(5.633)	0.160	9,18	(5.830)	0.155	9,18
H—O	(3.954)	0.239	8,19	(4.104)	0.233	8,19	(3.819)	0.240	8,19
H—O	(3.532)	0.247	9,19	(3.487)	0.258	9,19	(3.604)	0.242	9,19

The Cr(CO)₃ part of BCT was assumed to have three-fold symmetry with linear Cr—C—O chains. This assumption is in good agreement with spectroscopic investigations [4] which have established a threefold symmetry for the molecule. Because of these symmetry assumptions the plane of the oxygen atoms is parallel to the benzene plane.

Additional theoretical models involving mixtures of BCT(1) to BCT(5) were also investigated. BCT(1,2) is a mixture of 50% BCT(1) and 50% BCT(2). BCT(1,2,3) is a mixture of 25% of BCT(1), 25% of BCT(2) and of 50% of BCT(3); BCT(1,2,3,4,5) is a mixture of 12.5%, 12.5%, 25%, 25% and 25% of BCT(1), BCT(2), BCT(3), BCT(4) and BCT(5) respectively. Other concentrations within the various mixtures were also used and refined from the data as described below.

In the least squares analysis of the diffraction data [27,28], the following parameters were refined.

Bond distances (atom numbering from Fig. 8):

    C—H (between atoms 2-8, 3-9, 4-10, 5-11, 6-12 and 7-13)

    C—O (between atoms 14-17, 15-18, 16-19)

    C—C (between atoms 2-3, 3-4, 4-5, 5-6, 6-7 and 7-2)

    Cr—C(CO) (between atoms 1-14, 1-15, 1-16)

    Cr—C(benzene) (between atoms 1-2, 1-3, 1-4, 1-5, 1-6, 1-7)

Bond angles:

    ϕ (formed by bond distances 1-15, 1-14, 1-16 and the line connecting atom 1 and the center of the six-ring)

Mole fractions:

    For the models BCT(1,2) and BCT(1,2,3) mole-fractions, α_i, were refined by determining the relative concentrations of the components i of the different mixtures. Because of the magnitude of the calculations necessary, no such refinements were possible for BCT(1,2,3,4,5) for which only the statistical mixing-ratios were used.

    Together with the mentioned symmetry assumptions (six-fold symmetry for the planar six-ring, and three-fold symmetry for the Cr(CO)₃ groups) the above is a complete list of parameters needed to define the geometry of BCT. Torsional angles between ring and carbonyls were kept constant during model refinement in agreement with the definition of the models BCT(1) to BCT(5) given above.

Two different series of refinement were carried out. First only internal coordinates were refined for BCT(1), BCT(2) and BCT(3); and internal coordinates and mole fractions were refined for BCT(1,2) and BCT(1,2,3). All mean amplitudes of vibration were kept constant and the spectroscopic values of Table 1 were used. This procedure produced somewhat converged models with radial distribution curves shown in the Figs. 6 and 7 as the curves "with spectroscopic mean amplitudes".

In the next series of refinement, all amplitudes, internal coordinates, and mole fractions (where needed) were refined simultaneously. Amplitudes of different distances compressed in one peak of the radial distribution curve were refined in one group. Spectroscopic values were taken as starting values and the differences between them were retained.

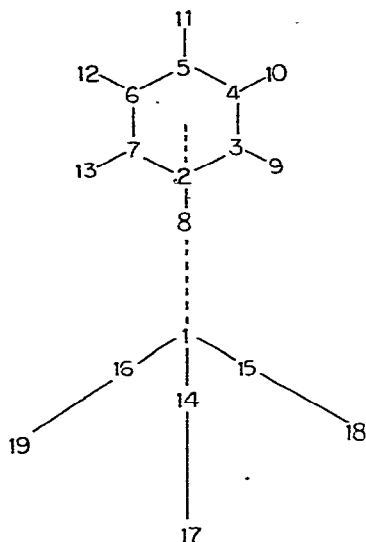Because of the size of the matrices involved, these total refinements were

Fig. 8. Benzenechromium tricarbonyl (BCT); atom numbering.

TABLE 2

STRUCTURAL PARAMETERS (DISTANCES AND MEAN AMPLITUDES; ALL VALUES IN Å) RE-
FINED BY LEAST SQUARES FOR BCT(1,2,3) AS DESCRIBED IN THE TEXT

Error limits are three times the standard deviations. Col. "NO. DIST" gives the distance numbers; col.
"Type" the distance type. The number in col. "CONF" assigns a particular distance to either BCT(1) or
BCT(2) or BCT(3). Col. "R" gives the internuclear distance between atoms i (col. "IATOM") and j (col.
"JATOM"); "U" gives the corresponding mean amplitude of vibration. All distances have a weight deter-
mined by the refined concentration of the corresponding conformation. The concentrations used to ob-
tain the values of this table were those listed in Table 4.

NO. DIST	Type	CONF	R	U	IATOM	JATOM
1	CR—C	1	2.2083(0.0055)	0.073(0.003)	1	2
2	CR—H	1	3.0346(0.0356)	0.181(0.007)	1	8
3	CR—C	1	1.8634(0.0051)	0.062(0.006)	1	14
4	CR—O	1	3.0163(0.0056)	0.059(0.007)	1	17
5	C—C	1	1.4167(0.0034)	0.047(0.005)	2	3
6	C—C	1	2.4537(0.0060)	0.053(0.003)	2	4
7	C—C	1	2.8333(0.0069)	0.063(0.017)	2	5
8	C—H	1	1.1011(0.0454)	0.078(0.007)	2	8
9	C—H	1	2.1862(0.0383)	0.100(0.003)	2	9
10	C—H	1	3.4515(0.0440)	0.119(0.025)	2	10
11	C—H	1	3.9345(0.0473)	0.091(0.031)	2	11
12	C—C	1	3.4762(0.0112)	0.129(0.025)	2	14
13	C—C	1	3.9712(0.0076)	0.084(0.031)	2	15
14	C—C	1	2.8979(0.0183)	0.103(0.017)	2	16
15	C—O	1	4.4745(0.0145)	0.102(0.127)	2	17
16	C—O	1	5.0978(0.0096)	0.109(0.066)	·2	18
17	C—O	1	3.7489(0.0234)	0.177(0.025)	2	19
18	H—C	1	4.0517(0.0277)	0.215(0.065)	8	14
19	H—C	1	4.7924(0.0357)	0.161(0.135)	8	15
20	H—C	1	3.1409(0.0241)	0.212(0.007)	8	16
21	H—O	1	4.9349(0.0214)	0.212(0.066)	8	17
22	H—O	1	5.9125(0.0313)	0.150(0.0)	8	18
23	H—O	1	3.7079(0.0275)	0.240(0.025)	8	19

TABLE 2 (continued)

NO. DIST	Type	CONF	R	U	IATOM	JATOM
24	C—C·	1	2.6020(0.0241)	0.102(0.003)	14	15
25	C—O	1	1.1529(0.0057)	0.037(0.007)	14	17
26	C—O	1	3.5055(0.0284)	0.161(0.025)	14	18
27	O—O	1	4.2118(0.0384)	0.182(0.065)	17	18
28	C—C	2	4.0423(0.0073)	0.151(0.065)	2	14
29	C—C	2	3.1553(0.0148)	0.151(0.007)	2	15
30	C—O	2	5.1875(0.0092)	0.104(0.066)	2	17
31	C—O	2	4.0713(0.0190)	0.191(0.065)	2	18
32	C—C	2	3.7699(0.0087)	0.130(0.025)	3	14
33	C—C	2	2.7978(0.0198)	0.099(0.017)	3	16
34	C—O	2	4.8441(0.0112)	0.115(0.066)	3	17
35	C—O	2	3.6237(0.0252)	0.193(0.025)	3	19
36	H—C	2	4.8970(0.0370)	0.157(0.066)	8	14
37	H—C	2	3.5544(0.0242)	0.218(0.025)	8	15
38	H—O	2	6.0496(0.0330)	0.143(0.0)	8	17
39	H—O	2	4.2697(0.0209)	0.250(0.065)	8	18
40	H—C	2	4.4943(0.0323)	0.140(0.127)	9	14
41	H—C	2	2.9752(0.0250)	0.220(0.007)	9	16
42	H—O	2	5.5205(0.0267)	0.163(0.0)	9	17
43	H—O	2	3.4797(0.0319)	0.251(0.025)	9	19
44	C—C	3	4.0243(0.0074)	0.141(0.065)	2	14
45	C—C	3	3.3140(0.0129)	0.104(0.025)	2	15
46	C—C	3	3.0124(0.0167)	0.133(0.007)	2	16
47	C—O	3	5.1649(0.0093)	0.105(0.066)	2	17
48	C—O	3	4.2705(0.0166)	0.159(0.065)	2	18
49	C—O	3	3.8922(0.0213)	0.108(0.031)	2	19
50	C—C	3	3.6312(0.0098)	0.151(0.025)	3	14
51	C—C	3	3.8851(0.0080)	0.086(0.031)	3	15
52	C—C	3	2.8236(0.0194)	0.111(0.017)	3	16
53	C—O	3	4.6695(0.0126)	0.108(0.135)	3	17
54	C—O	3	4.9892(0.0102)	0.113(0.066)	3	18
55	C—O	3	3.6559(0.0247)	0.176(0.025)	3	19
56	H—C	3	4.8707(0.0367)	0.157(0.066)	8	14
57	H—C	3	3.8024(0.0256)	0.158(0.031)	8	15
58	H—C	3	3.3268(0.0237)	0.221(0.025)	8	16
59	H—O	3	6.0151(0.0326)	0.143(0.0)	8	17
60	H—O	3	4.6026(0.0201)	0.182(0.135)	8	18
61	H—O	3	3.9616(0.0238)	0.221(0.031)	8	19
62	H—C	3	4.2865(0.0300)	0.195(0.065)	9	14
63	H—C	3	4.6653(0.0342)	0.144(0.135)	9	15
64	H—C	3	3.0182(0.0247)	0.206(0.007)	9	16
65	H—O	3	5.2462(0.0239)	0.195(0.066)	9	17
66	H—O	3	5.7456(0.0293)	0.158(0.0)	9	18
67	H—O	3	3.5391(0.0307)	0.245(0.025)	9	19

executed using only the diagonal terms of the matrix of derivatives. This is an approximate procedure, but nevertheless produced converged models, the parameters of which are given in Tables 2 and 3.

In a final step the refined parameters were further refined for a few cycles using the full matrix, in order to obtain the correlation matrices and the total square error sums of the Tables 4 and 5. When full matrix inversion was used, the mole ratios of mixtures could not be refined simultaneously with the other parameters because of the magnitude of the calculations. (See note added in proof at the end of the paper.)

Theoretical intensities corresponding to the parameters of the Tables 3 and 4 were used to calculate the corresponding theoretical RD-curves of the Figs. 6

TABLE 3

VALUES FOR SOME INTERNAL COORDINATES (DISTANCES IN Å, ANGLES IN DEGREES) FOR REFINED THEORETICAL MODELS OF BCT

For explanation of some of the symbols see text. Error limits are three times the standard deviations.

Bond distances	BCT(1)	BCT(2)	BCT(3)	BCT(1,2)	BCT(1,2,3)	BCT(1,2,3,4,5)
C–H	1.105 ± 0.053	1.090 ± 0.042	1.096 ± 0.047	1.088 ± 0.043	1.101 ± 0.045	1.100 ± 0.026
C–O	1.153 ± 0.007	1.150 ± 0.006	1.153 ± 0.006	1.154 ± 0.005	1.153 ± 0.006	1.152 ± 0.005
C–C	1.416 ± 0.004	1.417 ± 0.004	1.417 ± 0.004	1.415 ± 0.004	1.417 ± 0.003	1.416 ± 0.003
Cr–C(CO)	1.864 ± 0.006	1.859 ± 0.007	1.863 ± 0.005	1.863 ± 0.005	1.863 ± 0.005	1.863 ± 0.004
Cr–C(C_6H_6)	2.207 ± 0.006	2.209 ± 0.007	2.209 ± 0.006	2.209 ± 0.005	2.208 ± 0.006	2.208 ± 0.005
Bond angle						
ϕ	126.3 ± 1.0	126.5 ± 0.8	125.8 ± 0.9	126.5 ± 0.7	126.3 ± 0.7	126.2 ± 0.6

TABLE 4

TOTAL SQUARE ERROR SUMS $(V'PV)$ FOR VARIOUS REFINED MODELS OF BCT AND MOLE FRACTIONS OF REFINED MIXTURES[a]

Square error sums

	$V'PV$
BCT(1)	34.1
BCT(2)	47.4
BCT(3)	30.0
BCT(1,2)	29.9
BCT(1,2,3)	27.4
BCT(1,2,3,4,5)	28.9

Mole fractions

	BCT(1,2)	BCT(1,2,3)
BCT(1)	0.58 ± 0.31	0.30 ± 0.41
BCT(2)	0.42[b]	0.22 ± 0.50
BCT(3)		0.48[a]

[a] For more explanations concerning this table, see note added in proof at the end of the paper.
[b] Not refined. Mole fraction of this component was adjusted to obtain a total of 1.

and 7, and the refined theoretical intensities of BCT(1,2,3) were also used in Fig. 5.

Discussion of the results

The material presented in the Tables and Figures allows the following conclusions.

The C—C bond distance of the six-ring of BCT is slightly larger than in free benzene (1.417 ± 0.003 Å compared to 1.397 Å [29]). This is in good agreement with investigations of dibenzenechromium [30], for which the C—C bond length was found to be 1.423 Å. The bond elongation is probably due to the donation of electrons from the metal d-orbitals into benzene π-antibonding orbitals. This effect was predicted by SCFMO calculations [31].

The valence angle ϕ is consistently found to be above 120° (Table 3) in all the models tested. In general, Table 3 seems to indicate that the refinement of internal coordinates is not influenced significantly by the rotational state of the benzene ring. All internal coordinates are found within error limits for BCT(1), BCT(2), BCT(3) and the mixtures. We believe that the most reliable values are those refined for BCT(1,2,3), the model with the lowest error sum (Table 4).

The metal—carbon(ring) distances are found to be 2.208 ± 0.006 Å. This value is also very similar to the one found for dibenzenechromium (2.150 Å) [30]. The OC—Cr—CO angles are 88.6 ± 1.1°. This is close to 90° and reflects very well the nearly octahedral arrangement of bonds around the Cr atom.

As for the internal rotation of the benzene ring with respect to the carbonyls, the radial distribution curves shown in the Figs. 6 and 7 allow some very interesting conclusions. The curves which are based on spectroscopic mean amplitudes, show that no individual conformation with threefold symmetry can alone reproduce the experimental data. Both the staggered (BCT(1)) and eclipsed con-

TABLE 5. CORRELATION MATRIX FOR BCT(1,2,3)

Numbering of parameters is as follows: 1 = R[C(2)—C(3)], 2 = R[C(2)—H(8)], 3 = R[Cr—C(2)], 4 = φ, 5 = R[(Cr—C(14)], 6 = R[C(14)—O(17)], 7 = u[(Cr—C(2))], 8 = u[Cr—H(8)], 9 = u[Cr—C(14)], 10 = u[C(2)—C(3)], 11 = u[C(2)—C(3)], 12 = u[C(2)—C(5)], 13 = u[C(2)—H(8)], 14 = u[C(2)—H(10)], 15 = u[C(2)—H(11)], 16 = u[C(2)—O(18)], 17 = u[C(14)—H(8)], 18 = u[C(15)—H(8)]

	1	2	3	4	5	6	7	8	9
1	1.000								
2	0.202	1.000							
3	−0.419	−0.633	1.000						
4	−0.144	−0.019	−0.052	1.000					
5	0.177	0.283	−0.174	0.101	1.000				
6	−0.061	−0.442	0.303	0.116	0.431	1.000			
7	0.233	0.227	−0.312	−0.001	0.033	−0.156	1.000		
8	0.030	−0.029	0.015	0.118	0.034	0.049	0.087	1.000	
9	−0.071	0.017	0.069	−0.008	−0.035	−0.021	−0.063	−0.041	1.000
10	−0.079	−0.263	0.148	0.018	−0.025	0.126	0.006	−0.023	−0.015
11	0.039	−0.049	−0.005	0.004	−0.020	−0.003	0.115	0.531	−0.029
12	0.181	0.631	−0.398	−0.022	0.202	−0.332	0.123	0.027	−0.032
13	0.105	0.260	−0.187	−0.218	−0.048	−0.288	0.071	−0.096	0.007
14	−0.078	−0.035	0.029	0.323	−0.014	−0.001	−0.015	0.012	0.005
15	0.003	0.054	−0.019	0.214	0.057	0.008	0.011	0.038	−0.005
16	0.003	0.037	−0.028	0.037	0.007	−0.023	0.011	0.007	−0.002
17	−0.006	0.134	−0.065	0.437	0.107	−0.022	0.026	0.050	−0.000
18	−0.009	0.040	−0.015	0.232	0.045	0.008	0.008	0.038	−0.004

	10	11	12	13	14	15	16	17	18
10	1.000								
11	0.008	1.000							
12	−0.496	−0.000	1.000						
13	−0.069	−0.082	0.173	1.000					
14	0.018	−0.024	−0.027	0.165	1.000				
15	−0.023	0.005	0.042	0.035	0.201	1.000			
16	−0.013	0.003	0.026	0.004	0.006	0.159	1.000		
17	−0.035	−0.101	0.090	0.084	0.414	0.610	0.036	1.000	
18	−0.017	0.005	0.031	0.014	0.172	0.700	0.334	0.491	1.000

formations (BCT(2)) produce theoretical RD-curves which show significant deviations in the 4-6 Å range compared to the experiment. In contrast, a mixture of both (BCT(1,2)), produces a considerably improved RD-curve. (Note that deviations between theory and experiment in RD-curves for small distances are less serious than those for large distances. This is so because RD-curves provide distance probabilities divided by the magnitudes of the distances.)

A good qualitative agreement between theory and experiment is also found for the mixture of three components and intensities with spectroscopic mean amplitudes. But in this case, BCT(3) gives also a fair agreement alone, since its radial distribution represents, in effect, the mean of the radial distribution of a mixture of BCT(1) and BCT(2). This intermediate between the staggered and the eclipsed conformations of BCT cannot be accepted as a solution to the diffraction data, however, since it contradicts the spectroscopic investigations which have established a threefold molecular symmetry for this molecule [1,3,4].

When both amplitudes and internal coordinates are refined simultaneously, then a similar trend is again observed to favor the mixtures of several rotamers. While all theoretical models produce an improved fit to the experiment when refined this way, the mixtures show the lowest square error sums (Table 4). Again BCT(3) above is in good agreement with the experiment, but this model has to be rejected as an acceptable solution for the same reasons as before.

Moreover, the improved fit for BCT(1), BCT(2) and BCT(3) produced by amplitude refinement is achieved at the cost of adjusting mean amplitudes to values which are so different from the spectroscopic ones that the refined models are not satisfactory or even unacceptable.

u_{17-18} e.g. in BCT(1) is refined to be 0.287 Å. The calculated value is 0.166 Å. In BCT(1,2), BCT(1,2,3) and BCT(1,2,3,4,5) the refined values are 0.183 Å, 0.182 Å and 0.197 Å respectively, which is in better agreement with the calculated value.

Similar deviations are observed for most of the refined mean amplitudes of BCT(1), BCT(2) and BCT(3). (Models BCT(4) and BCT(5) were not refined individually in this way because of computing expenses but should give the same results since they are very similar to the others.) Most of the mean amplitudes of these individual conformations refined to values which are too large compared to the calculated ones. Refinement of unusually large mean amplitudes is a well established phenomenon in electron diffraction analysis, and is always observed when one tries to reproduce a composite peak of the radial distribution curve by one mean distance. The mean distance must be given an inflated mean amplitude to compensate for the other missing component distances, the radial distribution of which it is assumed to reproduce approximately. In good agreement with this interpretation, the mean amplitudes of vibration refined for the mixtures BCT(1,2) and BCT(1,2,3) are closer to the calculated values than the corresponding values for BCT(1), BCT(2) and BCT(3); and the values refined for mixtures are generally smaller than those refined for individual conformations.

All the features thus seem to indicate that benzenechromium tricarbonyl exists as a mixture of several conformations at 140°C in the vapor phase. The fact that BCT(1,2,3) and BCT(1,2,3,4,5) are the models with the lowest $V'PV$ seems to suggest that also states other than the eclipsed or staggered ones may be significantly populated. Mixing ratios (Table 4) are very uncertain. It is there-

fore not possible to calculate quantitatively differences of enthalpies or rotational energy barriers. All arguments above combined indicate, however, that benzenechromium tricarbonyl is essentially a nearly unhindered internal rotor in the vapor phase.

Note added in proof: As described in the text, the geometrical parameters for BCT were refined simultaneously with mean amplitudes of vibration and mole fractions using only diagonal terms of the matrix of derivatives in the least squares procedure because of the size of the problem. Due to improved computing facilities, an enlarged version of our least squares program could be adjusted to our computing system in the meantime. This made possible simultaneous full matrix refinements of all parameters.

The improved procedures did not produce any significant changes in the geometrical parameters given in the Tables 2 and 3. There were minor changes, however, in the calculated square error sums, $V'PV$, (Table 4) and the error limits of mole fractions increased (Table 4). The changes in $V'PV$ were in directions which further confirmed our conclusions. The values of Table 4 as shown now are those of the improved refinements.

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References

1 H.P. Fritz and J. Manchot, Spectrochim. Acta, 18 (1962) 171.
2 R. Cataliotti, A. Poletti and A. Santucci, J. Mol. Struc., 5 (1970) 215.
3 H.J. Buttery, G. Keeling, S.F.A. Kettle, I. Paul and P.J. Stamper, J. Chem. Soc. A, (1969) 2077.
4 L. Schäfer, G.M. Begun and S.J. Cyvin, Spectrochim. Acta, 28 (1972) 803.
5 P. Corradini and G. Allegra, J. Amer. Chem. Soc., 81 (1959) 2271.
6 M.F. Bailey and L.F. Dahl, Inorg, Chem., 4 (1965) 1314.
7 B. Rees and P. Coppens, J. Organometal. Chem., 42 (1972) C102.
8 O.L. Carter, A.T. McPhail and G.A. Sim, J. Chem. Soc. A, (1966) 822.
9 G.A. Sim, Ann. Rev. Phys. Chem., 18 (1967) 57.
10 B. Anderson, H.M. Seip, T.G. Strand and R. Stølevik, Acta Chem. Scand., 23 (1969) 3224.
11 L. Schäfer, A.C. Yates and R.A. Bonham, J. Chem. Phys., 55 (1971) 3055.
12 W. Schubert, J.F. Southern and L. Schäfer, J. Mol. Struc., 16 (1973) 403.
13 J. Brunvoll, S.J. Cyvin and L. Schäfer, J. Organometal. Chem., 36 (1972) 143.
14 S. Kjelstrup, S.J. Cyvin, J. Brunvoll and L. Schäfer, J. Organometal. Chem., 36 (1972) 137.
15 L. Schäfer, J.F. Southern and S.J. Cyvin, Spectrochim. Acta A, 27 (1971) 1083.
16 L.H. Jones, R.S. McDowell and M. Goldblatt, Inorg. Chem., 8 (1969) 2349.
17 W.D. Gwinn, J. Chem. Phys., 55 (1971) 477.
18 R. Stølevik, H.M. Seip and S.J. Cyvin, Chem. Phys. Lett., 15 (1972) 263.
19 L. Schäfer, J.D. Ewbank, S.J. Cyvin and S.J. Brunvoll, J. Mol. Struc., 14 (1972) 185.
20 L. Schäfer, S.J. Cyvin and J. Brunvoll, Chem. Phys. Lett., 15 (1972) 505.
21 L. Schäfer, S.J. Cyvin and J. Brunvoll, Tetrahedron, 27 (1971) 6177.
22 J. Brunvoll, S.J. Cyvin and L. Schäfer, Acta Chem. Scand., 24 (1970) 3427.
23 S.J. Cyvin, B.N. Cyvin, J. Brunvoll and L. Schäfer, Acta Chem. Scand., 24 (1970) 3420.
24 L. Schäfer, J. Mol. Struc., 22 (1974) 321.
25 L.H. Ngai, F.E. Stafford and L. Schäfer, J. Amer. Chem. Soc., 91 (1969) 48.
26 L. Schäfer, J.F. Southern, S.J. Cyvin and J. Brunvoll, J. Organometal. Chem., 24 (1970) C13.
27 K. Hedberg and M. Iwasaki, Acta Cryst., 17 (1964) 529.
28 O. Bastiansen, L. Hedberg and K. Hedberg, J. Chem. Phys., 27 (1957) 1311.
29 A. Almenningen, O. Bastiansen and L. Fernholt, Kgl. Norske Videnskab. Selskabs, Skrifter (1958) No. 3.
30 A. Haaland, Acta Chem. Scand., 19 (1965) 41.
31 E.M. Shustorovich and M.E. Dyatkina, J. Struc. Chem. USSR Engl. Transl., 2 (1961) 40.
32 N.S. Chiu, Master's thesis, University of Arkansas, 1975.