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THE CRYSTAL STRUCTURE OF TRICARBONYLANTHRACENE-CHROMIUM

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INTRODUCTION

In recent years structural studies on tricarbonylarenechromium complexes have provided information relevant to the problem of the distribution of the π-electrons in the aromatic rings bonded to the $Cr(CO)_3$ group. No significant alternation of long and short C–C bonds in the aromatic rings could be deduced from X-ray diffraction studies of the tricarbonylchromium complexes of benzene[1,2], hexamethylbenzene[3], phenanthrene (orthorhombic modification)[4], or 9,10-dihydrophenanthrene[4] in which complexes the $Cr(CO)_3$ group takes up a staggered orientation with respect to the carbon atoms of the arene, nor was any observed in the complexes with *o*-toluidine[5] or anisole[6], the latter in the charge-transfer complex with 1,3,5-trinitrobenzene, where the $Cr(CO)_3$ group is rotated roughly through 60°. The π-electrons in the aromatic rings appear to be completely delocalised. No conclusions could be drawn from the bond lengths of a monoclinic modification of tricarbonylphenanthrenechromium which used projection data only[7].

The object of the present work was a detailed structural study, by X-ray examination of the solid form, of the anthracene molecule in the complex tricarbonylanthracenechromium. The NMR spectrum of the compound, which had been prepared by the direct reaction of anthracene with chromium hexacarbonyl[8], had been interpreted[8] in favour of bonding of the chromium to the end ring of the organic ligand. A similar geometric arrangement has been found in both the orthorhombic and monoclinic forms of tricarbonylphenanthrenechromium[4,7].

EXPERIMENTAL

Crystal data

$C_{17}H_{10}O_3Cr$ (mol. wt. 314.2), orthorhombic, $a=13.36\pm0.04$, $b=15.95\pm0.06$, $c=12.94\pm0.03$ Å, $U=2757$ Å^3, $D_c=1.51_4$ for $Z=8$, spacegroup *Pbca* (D_{2h}^{15}, No. 61) by systematic absences. For Mo-K_α radiation ($\lambda=0.7107$ Å), $\mu=8.6$ cm^{-1}.

The prismatic crystals were dark violet, diamagnetic and soluble in organic solvents. Altogether 2432 diffracted intensities were measured with a Hilger and Watts linear diffractometer fitted with scintillation counter, and with Mo-K_α radiation and balanced-filter operation. The unit cell dimensions had been determined previously from precession and Weissenberg techniques. The intensities were corrected for background but no absorption corrections were applied since for the crystal used these were negligible. The different layers obtained about the *b* axis were brought to a common scale by comparison with 0*kl* and 2*kl* reflexions. The statistical method of Wilson[9] was used to put the combined intensities on an approximately absolute scale and to determine the value of the overall temperature exponent.

Determination of the structure

The structure was solved by the heavy atom method. The chromium atom positions were determined from Patterson syntheses and the signs of structure factors calculated from these positions were used in a three-dimensional Fourier synthesis. The synthesis showed the positions of all the light atoms in the unit cell, excluding hydrogen.

Refinement of the structural parameters has been carried out by two different least-squares procedures: (*i*) by a block-diagonal approximation* and a weighting scheme discussed by Cruickshank[10] and (*ii*) a full-matrix scheme* with weights $w^{-1} = 1 + 0.005\ F_o^2$. Both isotropic and anisotropic refinements were carried out. The block-diagonal anisotropic refinement resulted in a mean C–C bond length of 1.416 Å whilst the isotropic full-matrix refinement, after three cycles, gave a mean value of 1.417 Å. Standard deviations in both cases lay in the region 0.011–0.017 Å. After introduction of the ten hydrogen atoms, at calculated positions, the mean bond length in the anthracene ring shortened to 1.411 Å. This is a result of the mathematical treatment whereby the least-squares refinement of the model which did not include

TABLE 1

ATOMIC COORDINATES OF TRICARBONYLANTHRACENECHROMIUM

Atom	x/a	σ_x	y/b	σ_y	z/c	σ_z
Cr	0.0673	0.0001	0.1787	0.0001	0.2018	0.0001
O(1)	−0.0497	0.0006	0.1429	0.0006	0.3917	0.0006
O(2)	−0.0381	0.0007	0.3444	0.0005	0.1941	0.0007
O(3)	0.2259	0.0006	0.2636	0.0006	0.3275	0.0006
C(1)	0.1789	0.0007	0.0842	0.0006	0.1521	0.0007
C(2)	0.1805	0.0007	0.1515	0.0006	0.0807	0.0007
C(3)	0.0899	0.0007	0.1764	0.0006	0.0323	0.0007
C(4)	0.0006	0.0006	0.1272	0.0005	0.0471	0.0006
C(5)	−0.0894	0.0007	0.1460	0.0005	−0.0055	0.0007
C(6)	−0.1738	0.0006	0.0976	0.0005	0.0100	0.0006
C(7)	−0.2648	0.0008	0.1124	0.0007	−0.0468	0.0008
C(8)	−0.3490	0.0007	0.0641	0.0008	−0.0306	0.0008
C(9)	−0.3470	0.0007	−0.0012	0.0007	0.0431	0.0008
C(10)	−0.2636	0.0007	−0.0173	0.0006	0.0990	0.0007
C(11)	−0.1741	0.0006	0.0310	0.0005	0.0846	0.0006
C(12)	−0.0865	0.0006	0.0134	0.0005	0.1379	0.0006
C(13)	0.0030	0.0006	0.0598	0.0005	0.1221	0.0006
C(14)	0.0921	0.0006	0.0427	0.0005	0.1765	0.0006
C(15)	−0.0034	0.0007	0.1554	0.0006	0.3191	0.0007
C(16)	0.1636	0.0008	0.2302	0.0006	0.2772	0.0007
C(17)	0.0030	0.0008	0.2801	0.0006	0.1942	0.0008

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* We have used the programmes written by J. J. Daly, F. S. Stephens and P. J. Wheatley for the Elliott 803 and by L. I. Hodgson, O. S. Mills and F. S. Stephens for the Atlas computer.

TABLE 2

ANISOTROPIC TEMPERATURE FACTOR COEFFICIENTS

Atom	$B_{11}\cdot 10^5$	$B_{22}\cdot 10^5$	$B_{33}\cdot 10^5$	$B_{12}\cdot 10^5$	$B_{13}\cdot 10^5$	$B_{23}\cdot 10^5$
Cr	456 (7)	313 (6)	440 (8)	23 (5)	53 (6)	50 (5)
O(1)	931 (56)	667 (43)	692 (51)	81 (40)	345 (44)	1 (38)
O(2)	1142 (71)	436 (37)	1238 (80)	156 (41)	213 (60)	24 (41)
O(3)	836 (54)	820 (51)	860 (58)	295 (43)	25 (45)	321 (44)
C(1)	667 (58)	414 (41)	505 (51)	129 (38)	11 (45)	83 (36)
C(2)	543 (52)	465 (44)	638 (62)	48 (38)	161 (47)	135 (41)
C(3)	561 (52)	433 (41)	515 (53)	32 (35)	174 (42)	98 (36)
C(4)	576 (49)	345 (35)	374 (43)	40 (32)	4 (38)	50 (30)
C(5)	692 (57)	311 (35)	489 (51)	11 (34)	15 (42)	7 (32)
C(6)	529 (47)	314 (35)	506 (50)	51 (51)	20 (40)	43 (31)
C(7)	738 (65)	475 (45)	768 (70)	277 (44)	235 (55)	158 (46)
C(8)	527 (55)	679 (59)	745 (73)	62 (46)	148 (53)	79 (53)
C(9)	556 (55)	603 (54)	751 (70)	16 (44)	6 (51)	242 (50)
C(10)	496 (50)	376 (38)	750 (53)	5 (34)	41 (46)	127 (39)
C(11)	506 (47)	349 (36)	530 (50)	55 (31)	30 (40)	81 (33)
C(12)	589 (51)	315 (34)	485 (50)	14 (31)	7 (40)	15 (31)
C(13)	486 (44)	287 (34)	526 (50)	35 (30)	15 (38)	43 (30)
C(14)	489 (46)	285 (33)	574 (54)	28 (29)	5 (39)	41 (32)
C(15)	579 (52)	394 (40)	470 (51)	33 (35)	178 (42)	11 (33)
C(16)	728 (62)	411 (43)	663 (63)	87 (40)	59 (51)	105 (40)
C(17)	850 (70)	388 (42)	645 (66)	17 (43)	206 (56)	52 (40)

hydrogen atoms resulted in the carbon atoms being moved towards the points of gravity of the C–H bonds.

Table 1 shows the final atomic coordinates, together with their estimated standard deviations, after full-matrix anisotropic refinement in which hydrogen atoms had been included but whose positions had not been refined. After five cycles of this refinement the reliability factor, $R = \{\Sigma||F_o|-|F_c||\}/\Sigma|F_o|$, had decreased to 0.095 for 2016 reflexions and to 0.112 for the 2432 reflexions when all the very weak and zero intensity reflexions were included. Table 2 lists the anisotropic temperature factor coefficients, B_{ij}, together with their estimated standard deviations. The RMS am-

TABLE 3

RMS AMPLITUDES AND DIRECTIONAL COSINES

Atom	*i*	U_i	*p*	*q*	*r*
Cr	1	0.209	0.7381	−0.4828	0.4712
	2	0.197	0.6380	0.7266	−0.2549
	3	0.188	−0.2193	0.4888	0.8444
O(1)	1	0.306	−0.8077	0.4736	−0.3511
	2	0.290	−0.4084	−0.8790	−0.2461
	3	0.227	−0.4252	−0.0554	0.9034
O(2)	1	0.337	0.6925	0.0851	0.7163
	2	0.310	−0.6984	−0.1696	0.6953
	3	0.233	−0.1806	0.9818	0.0580
O(3)	1	0.343	0.3279	−0.8872	0.3247
	2	0.275	0.7663	0.0488	−0.6406
	3	0.247	0.5525	0.4589	0.6959
C(1)	1	0.255	0.8282	0.5463	−0.1250
	2	0.225	0.5480	−0.7427	0.3850
	3	0.203	−0.1175	0.3873	0.9144
C(2)	1	0.258	0.3415	−0.7296	0.5925
	2	0.229	0.5493	0.6665	0.5040
	3	0.209	0.7626	−0.1533	−0.6284
C(3)	1	0.245	0.4999	−0.7354	0.4575
	2	0.228	0.7161	0.6481	0.2592
	3	0.195	−0.4871	0.1980	0.8506
C(4)	1	0.229	0.9639	0.2650	−0.0263
	2	0.211	0.2649	−0.9437	0.1982
	3	0.177	−0.0277	0.1980	0.9798
C(5)	1	0.250	0.9992	0.0257	−0.0305
	2	0.204	0.0224	0.2707	0.9624
	3	0.200	−0.0329	0.9623	−0.2699
C(6)	1	0.222	0.9016	0.3511	−0.2527
	2	0.208	0.3697	−0.3219	0.8716
	3	0.197	0.2247	−0.8793	−0.4200
C(7)	1	0.295	−0.6617	−0.5450	0.5149
	2	0.239	0.3815	0.3464	0.8570
	3	0.221	0.6454	−0.7635	0.0213
C(8)	1	0.297	0.0578	−0.9873	0.1477
	2	0.255	−0.3646	0.1169	0.9238
	3	0.212	−0.9294	−0.1073	−0.3532
C(9)	1	0.292	0.0173	−0.8616	0.5073
	2	0.237	−0.1101	0.5027	0.8575
	3	0.224	0.9938	0.0707	0.0861
C(10)	1	0.257	0.0824	−0.3491	0.9334
	2	0.215	−0.2524	−0.9134	−0.3194
	3	0.211	0.9641	−0.2093	−0.1634
C(11)	1	0.226	−0.5086	−0.6502	0.5644
	2	0.210	0.8200	−0.1659	0.5478
	3	0.201	0.2626	−0.7414	−0.6175
C(12)	1	0.231	0.9980	0.0596	0.0199
	2	0.204	0.0180	−0.5752	0.8178
	3	0.200	0.0602	−0.8159	−0.5751
C(13)	1	0.214	−0.5479	−0.3077	0.7779
	2	0.209	0.8112	0.0316	0.5839
	3	0.190	0.2043	−0.9510	−0.2323
C(14)	1	0.222	0.0107	−0.1732	0.9848
	2	0.211	0.9821	−0.1836	−0.0430
	3	0.190	−0.1882	−0.9676	−0.1681
C(15)	1	0.238	0.8626	−0.2966	0.4098
	2	0.224	0.2606	0.9549	0.1426
	3	0.190	−0.4336	−0.0162	0.9010
C(16)	1	0.262	0.8644	−0.3716	0.3387
	2	0.240	−0.4821	−0.4215	0.7681
	3	0.220	−0.1426	−0.8272	−0.5435
C(17)	1	0.283	0.9422	−0.0023	0.3350
	2	0.232	−0.2650	−0.6167	0.7413
	3	0.219	−0.2049	0.7872	0.5816

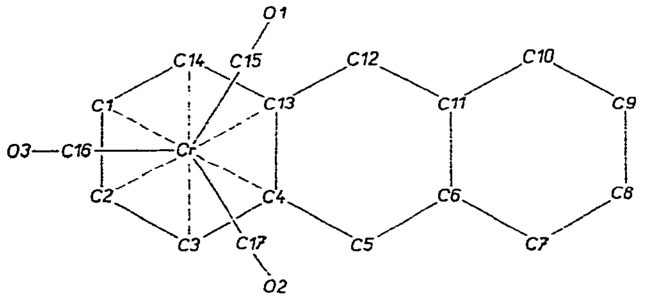

Fig. 1.

TABLE 4

MOLECULAR GEOMETRY

Intramolecular distances and estimated standard deviations (Å)			
C(1)–C(2)	1.416(14)	Cr–C(1)	2.217(9)
C(1)–C(14)	1.372(13)	Cr–C(2)	2.221(9)
C(2)–C(3)	1.420(14)	Cr–C(3)	2.215(9)
C(3)–C(4)	1.442(12)	Cr–C(4)	2.340(8)
C(4)–C(5)	1.413(12)	Cr–C(13)	2.324(8)
C(4)–C(13)	1.449(12)	Cr–C(14)	2.219(8)
C(5)–C(6)	1.380(12)	Cr–C(15)	1.826(10)
C(6)–C(7)	1.441(12)	Cr–C(16)	1.812(10)
C(6)–C(11)	1.435(12)	Cr–C(17)	1.834(10)
C(7)–C(8)	1.380(16)	C(15)–O(1)	1.142(10)
C(8)–C(9)	1.413(16)	C(16)–O(3)	1.184(12)
C(9)–C(10)	1.354(14)	C(17)–O(2)	1.163(13)
C(10)–C(11)	1.435(12)	C(12)–C(13)	1.421(12)
C(11)–C(12)	1.387(12)	C(13)–C(14)	1.410(11)
Intramolecular angles and estimated standard deviations (°)			
C(2)–C(1)–C(14)	121.9(6)	C(15)–Cr–C(16)	90.7(4)
C(1)–C(2)–C(3)	119.2(6)	C(15)–Cr–C(17)	89.0(3)
C(2)–C(3)–C(4)	119.7(7)	C(16)–Cr–C(17)	87.9(4)
C(3)–C(4)–C(13)	118.3(6)	Cr–C(15)–O(1)	177.8(9)
C(5)–C(4)–C(13)	119.4(8)	Cr–C(16)–O(3)	179.3(9)
C(4)–C(5)–C(6)	120.4(8)	Cr–C(17)–O(2)	177.0(9)
C(5)–C(6)–C(11)	120.9(6)	C(6)–C(11)–C(10)	119.2(3)
C(7)–C(6)–C(11)	117.5(6)	C(6)–C(11)–C(12)	118.8(4)
C(6)–C(7)–C(8)	121.3(6)	C(11)–C(12)–C(13)	122.2(8)
C(7)–C(8)–C(9)	119.9(7)	C(4)–C(13)–C(12)	117.6(5)
C(8)–C(9)–C(10)	121.1(7)	C(1)–C(14)–C(13)	120.4(6)
C(9)–C(10)–C(11)	121.0(5)	C(4)–C(13)–C(14)	119.8(4)

plitudes, U_i, and the directional cosines (p,q,r) of the principal axes of the vibrational ellipsoids with respect to the crystallographic axes are listed in Table 3. The oxygen atoms are subject to the greatest amount of vibration. Table 4 summarizes the most important intramolecular bond lengths and bond angles. A schematic view of the molecule, with numbering scheme is shown in Fig. 1 and a general view of the molecule in Fig. 2.

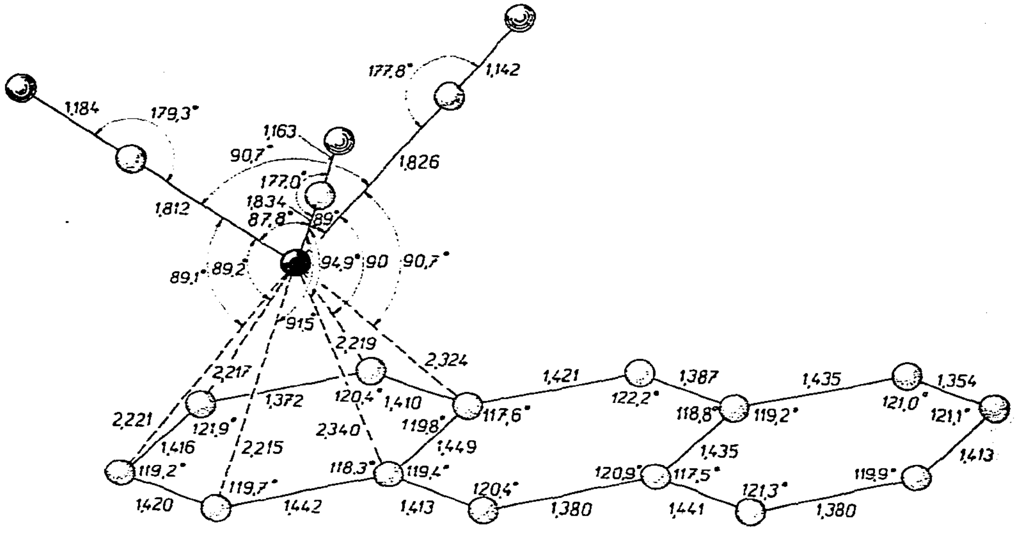

Fig. 2.

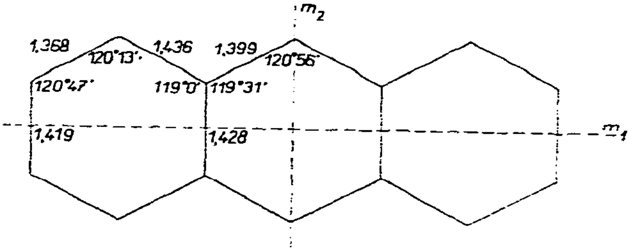

Fig. 3.

DISCUSSION

As in the phenanthrene compound, the $Cr(CO)_3$ group is attached to the side ring of the anthracene molecule. The C–C bond lengths in the bonded anthracene molecule differ only slightly from those found in the free anthracene molecule[11] (Fig. 3). A small, but significant, lengthening of C–C bonds exists in that half of the molecule which includes the bonded $Cr(CO)_3$ group. Thus the mean C–C distance for this half is 1.418 Å whereas the mean length in the non-bonded half is 1.403 Å. Whereas in the free anthracene molecule each ring has an average C–C length of 1.409 Å, in the complex the average value increases in each ring in the direction non-bonded to bonded ring from 1.410 to 1.418 Å.

It is also instructive to compare the means of the two sets of alternate bond lengths in the complexed and free ligand. In the ring bonded to the chromium atom the average of the lengths C(1)–C(14), C(2)–C(3) and C(4)–C(13) is 1.414 Å and that of C(1)–C(2), C(3)–C(4) and C(13)–C(14) is 1.423 Å. The corresponding means in the other side ring are 1.390 Å for C(6)–C(11), C(7)–C(8) and C(9)–C(10), and 1.430 Å for C(6)–C(7), C(8)–C(9) and C(10)–C(11). These values are very close to the equivalent sets of alternate bond lengths in free anthracene *viz.* 1.388 and 1.430 Å[11]. This shows that there are insignificant structural changes in the non-bonded side ring of anthracene as a result of the coordination. The effect of coordination upon the bonded ring is, if anything, to cause the alternate bond lengths to become more equal.

The bonded anthracene ligand is no longer strictly planar. It folds along the line m_2 (Fig. 3) into two planar halves which are tilted at 3.2° to one another (see Table 5).

TABLE 5

BEST LEAST-SQUARES PLANES DEFINED BY ATOMIC POSITIONS

In the following equations *X*, *Y*, *Z* refer to the atomic coordinates expressed in Angstroms

(*i*) Plane defined by all the carbon atoms of the anthracene ligand:

$$0.2751\,X - 0.6372\,Y - 0.7199\,Z + 1.7061 = 0$$

Deviations of atoms from this plane (Å):

C(1)	0.091	C(6)	−0.018	C(11)	−0.037
C(2)	0.078	C(7)	0.026	C(12)	−0.033
C(3)	−0.057	C(8)	0.057	C(13)	−0.028
C(4)	−0.023	C(9)	0.041	C(14)	−0.033
C(5)	−0.055	C(10)	−0.009	Cr	−1.743

(*ii*) Plane defined by the "bonded half" carbon atoms of the anthracene ligand, *viz.* C(1)–C(5), C(12)–C(14):

$$0.02466\,X - 0.6371\,Y - 0.7303\,Z + 1.7436 = 0$$

Deviations of atoms from this plane (Å):

C(1)	0.040	C(4)	0.008	C(13)	−0.008
C(2)	0.036	C(5)	0.017	C(14)	−0.055
C(3)	−0.058	C(12)	0.019	Cr	−1.757

(*iii*) Plane defined by the "non-bonded half" carbon atoms of the anthracene ligand, *viz.* C(5)–C(12):

$$0.2999\,X - 0.6353\,Y - 0.7116\,Z + 1.7762 = 0$$

Deviations of atoms from this plane (Å):

C(5)	−0.011	C(8)	0.010	C(11)	−0.014
C(6)	−0.001	C(9)	0.001	C(12)	0.024
C(7)	0.007	C(10)	−0.016	Cr	−1.623

The chromium is not bonded uniformly to all six carbon atoms of the ring. Four Cr–C distances occur at 2.215, 2.217, 2.219 and 2.221 Å whereas the remaining two are significantly longer at 2.324 and 2.340 Å. The displacement is away from the centre of the ligand. The perpendicular distance from the chromium to the plane of the side ring of the anthracene is 1.76 Å. A similar tendency for the formation of four shorter and two longer Cr–C contacts was observed also in the phenanthrene complex[4]. At the same time the C–C bond lengths in the middle ring adjacent to the bonded ring are increased compared with the pair adjacent to the non-bonded ring.

The $Cr(CO)_3$ group has the staggered conformation with the carbonyl–chromium vectors directed towards the midpoints of the ring C–C bonds. The Cr–C distances, 1.812, 1.826 and 1.834 Å, are significantly shorter than the values found in $Cr(CO)_6$ and indicate enhanced back-donation to the carbonyl groups as a result of replacement of three carbonyls by the anthracene ligand. The three carbonyl groups form a pyramidal arrangement with C–Cr–C bond angles close to 90° *viz.* 87.8, 89.0 and 90.7°.

The C–O distances are typical of terminal-bonded carbonyls namely 1.142, 1.163 and 1.184 Å. They are also nearly linear with deviations of 0.7, 2.2 and 3.0°. The shortest intermolecular contact is between C(9) ... O(1), 3.276 Å. Five other contacts are less than 3.6 Å.

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SUMMARY

The structure of tricarbonylanthracenechromium has been examined by X-ray analysis of the solid. The dark violet crystals are orthorhombic with $a = 13.36$, $b = 15.95$, $c = 12.94$ Å, spacegroup *Pbca* with eight molecules per unit cell. When compared with the structure of the free ligand, the bonded anthracene shows a small increase in the average C–C bond lengths in the end ring to which the chromium is attached. The changes in bond lengths in this ring are such to make the alternate bond lengths more equal than in free anthracene. The ligand is also slightly folded, by about 3°, across the central ring. The chromium atom is not precisely equidistant to the six carbons of the end ring, but is symmetrically displaced parallel to the ligand so that four short and two long Cr–C distances result, average values 2.224 and 2.338 Å.

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