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The Molecular Structure of Tricarbonyl(triple-layered [2.2]-paracyclophane)chromium at −95°C(Monoclinic Form) and −160°C (Triclinic Form)†

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The tricarbonylchromium complex of triple-layered [2.2]paracyclophane shows a reversible phase transition in the solid state from the monoclinic to the triclinic form at a temperature between −100 and −110 °C. The monoclinic form crystallizes in the space group $P2_1/c$, with a=15.095(6), b=9.950(3), c=15.641(5) Å, β=103.46(3)° (−95 °C), and Z=4: The triclinic form belongs to the space group $P\bar{1}$, with a=15.037(5) Å, b=9.913(2), c=15.662(5) Å, α=89.41(3), β=104.51(3), γ=89.39(4)° (−160 °C), and Z=4. In the triclinic crystal, two molecules are crystallographically independent. The crystal structures were solved by the direct method and then refined by the block-diagonal least-squares procedure to the R indices of 0.067 for 3530 (monoclinic form) and 0.079 for 6776 (triclinic form) observed reflections. No essential difference is found between the structures of the monoclinic-form molecule and the two triclinic-form molecules. The interlayer distance between the upper-layer benzene ring coordinated to the $Cr(CO)_3$ group and the middle-layer benzene ring is unusually shorter than the corresponding distance between the middle- and lower-layer benzene rings. No bond alternation is found in the upper-layer benzene ring, unlike as in the tricarbonyl(benzene)chromium complex and the (tricarbonyl)chromium complex of double-layered [2.2]paracyclophane. The phase transition of the crystal can be explained by a slight change in the molecular packing.

In a series of structural studies of layered cyclophanes, the X-ray structure determination of the (tricarbonyl)chromium complex of double-layered [2.2]-paracyclophane (TCPC).[1] has been carried out. The molecular structure of TCPC showed an unusual shortening of the distance between two benzene rings compared with the corresponding distances in other double-layered [2.2]paracyclophanes, [2.2]paracyclophane (PC),[2] 4,7,13,16-tetramethyl[2.2]paracyclophane (TMPC),[3] and 4,7-dimethyl[2.2]paracyclophane (DMPC).[3] Stimulated by this interesting feature of the [2.2]paracyclophane structure, we then determined the molecular structure of the (tricarbonyl)chromium complex of triple-layered [2.2]paracyclophane (TC3PC) by means of X-ray diffraction. A low-temperature experiment on the TC3PC revealed a reversible phase transition between the monoclinic and triclinic forms. The molecular structures determined are compared with that of 12-bromo(triple-layered [2.2]paracyclophane) (BR3PC),[4] which is the only example of a triple-layered [2.2]paracyclophane whose structure has been determined by the X-ray diffraction method.

Experimental

All the X-ray measurements were undertaken on a Rigaku automated, four-circle diffractometer with graphite-monochromatized Mo$K\alpha$ radiation. A Rigaku low-temperature apparatus was attached to the diffractometer, and the low temperature was attained by the gas-flow method of liquid nitrogen. During the process of cooling the crystal down to −160 °C from room temperature, an interesting phase transition has been found. At a temperature between −100 and −110 °C, the split and complexity of the diffraction profile of the monitor reflections were observed. At temperature below −110 °C, the profile of the same diffraction became sharp and simple again. These changes were observed reversibly. The process of the phase transition was confirmed by the oscillation photographs which were taken on the four-circle diffractometer by the use of a special film-cassette and ω-oscillation mechanism. It was revealed that the crystal belongs to the monoclinic system at −80 °C and to the triclinic system at −130 °C. The X-ray diffraction data have been collected at −95 °C for the monoclinic form and at −160 °C for the triclinic form with the same crystal. The crystal data are listed in Table 1. The triclinic form has two crystallographically independent molecules per unit cell.

The integrated intensities were measured by the θ-2θ scan technique at a 2θ scan rate of 4° min^{-1} in the range of $\Delta 2\theta=(2.0+0.7\tan\theta)°$. The backgrounds were counted for 5 s before and after the scan of each peak. Totals of 3530 and 6776 observed reflections [$|F_o|>3\sigma(F_o)$] were collected up to 2θ=54 and 50° for the monoclinic and triclinic forms respectively. The intensity data were corrected for the usual Lorentz and polarization effects, but not for the absorption [μ(Mo$K\alpha$)=5.5 and 5.6 cm^{-1} for monoclinic and triclinic crystals].

Structure Solution and Refinement

The crystal structures of the monoclinic and triclinic forms of TC3PC were solved by the direct method (*MULTAN* 78)[5] and were refined by the block-diagonal least-squares procedure (*HBLS* V),[6] with anisotropic temperature factors for nonhydrogen atoms and isotropic temperature factors for hydrogen atoms. The final R indices are 0.067 and 0.079 (R_W=0.083 and 0.135) for 3530 and 6776 observed reflections of the monoclinic and triclinic forms respectively. The weighting scheme used was $w=\{\sigma^2(F_o)+a|F_o|+b|F_o|^2\}^{-1}$. The weighting parameters

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Table 1. Crystal Data of Tricarbonyl(triple-layered [2.2]paracyclophane)chromium

Formula	$C_{29}H_{26}O_3Cr$	
Formula Weight	474.5	
$F(000)$	992	
Temperature/°C	−95	−160
System	Monoclinic	Triclinic
Space Group	$P2_1/c$	$P\bar{1}$
a/Å	15.095(6)	15.037(5)
b/Å	9.950(3)	9.913(2)
c/Å	15.641(5)	15.662(5)
α/°		89.41(3)
β/°	103.46(3)	104.51(3)
γ/°		89.39(4)
V/Å^3	2284.8(13)	2259.8(12)
Z	4	4
D_c/g cm^{-3}	1.379	1.394
D_m/g cm^{-3}	1.37 (room temp)	
μ(Mo $K\alpha$)/cm^{-1}	5.54	5.60

Table 2. Final Atomic Parameters for Nonhydrogen Atoms together with the Estimated Standard Deviations in Parentheses

Monoclinic Form (at −95°C):

Atom	x	y	z	B_{eq}/Å^2[7]
Cr	0.79662(5)	0.23301(7)	0.83800(4)	1.83
O(1)	0.8871(3)	0.2405(4)	1.0301(3)	4.4
O(2)	0.6440(3)	0.0540(5)	0.8607(3)	4.6
O(3)	0.8996(3)	-0.0192(4)	0.8222(3)	3.7
C(1)	0.5768(4)	0.4531(5)	0.6031(4)	3.2
C(2)	0.5906(4)	0.3374(6)	0.6747(4)	4.4
C(3)	0.6870(4)	0.3395(5)	0.7298(3)	2.9
C(4)	0.7080(3)	0.4114(5)	0.8099(3)	2.6
C(5)	0.7964(3)	0.4529(4)	0.8454(3)	2.3
C(6)	0.8667(3)	0.4279(4)	0.8008(3)	2.0
C(7)	0.8480(4)	0.3353(4)	0.7311(3)	2.3
C(8)	0.7600(4)	0.2900(5)	0.6964(3)	2.7
C(9)	0.9482(3)	0.5188(5)	0.8142(4)	2.8
C(10)	0.9229(3)	0.6557(5)	0.7616(3)	2.6
C(11)	0.8293(3)	0.6520(4)	0.6996(3)	2.1
C(12)	0.8136(3)	0.5944(5)	0.6145(3)	2.2
C(13)	0.7292(4)	0.5352(5)	0.5830(3)	2.5
C(14)	0.6551(3)	0.5532(5)	0.6221(3)	2.3
C(15)	0.6638(3)	0.6570(5)	0.6846(3)	2.5
C(16)	0.7522(3)	0.6938(5)	0.7273(3)	2.3
C(17)	0.5832(4)	0.7392(5)	0.6991(4)	3.3
C(18)	0.5487(4)	0.8456(6)	0.6238(4)	3.9
C(19)	0.6211(4)	0.8760(5)	0.5735(4)	2.9
C(20)	0.7004(4)	0.9458(5)	0.6127(4)	3.0
C(21)	0.7810(4)	0.9233(5)	0.5869(3)	2.9
C(22)	0.7838(4)	0.8316(5)	0.5188(3)	2.9
C(23)	0.7007(4)	0.7878(5)	0.4686(3)	3.4
C(24)	0.6214(4)	0.8091(6)	0.4954(4)	3.4
C(25)	0.8732(4)	0.7621(6)	0.5174(4)	3.6
C(26)	0.8778(4)	0.6135(5)	0.5537(3)	3.2
C(27)	0.8510(4)	0.2355(5)	0.9561(3)	2.8
C(28)	0.7030(4)	0.1244(6)	0.8539(3)	3.1
C(29)	0.8605(3)	0.0797(5)	0.8277(3)	2.5

Table 2. (Continued 1)

Triclinic Form (at −160°C):
Molecule 1

Atom	x	y	z	B_{eq}/Å^2
Cr	0.78752(6)	0.23825(9)	0.83997(6)	1.12
O(1)	0.8889(4)	0.2405(5)	1.0315(3)	2.4
O(2)	0.8871(4)	-0.0164(5)	0.8160(4)	2.4
O(3)	0.6351(4)	0.0616(6)	0.8654(4)	3.0
C(1)	0.9138(4)	0.6508(6)	0.7512(4)	1.6
C(2)	0.9426(4)	0.5134(7)	0.8028(5)	1.9
C(3)	0.8577(4)	0.4268(6)	0.7971(4)	1.2
C(4)	0.8293(5)	0.3357(6)	0.7282(4)	1.8
C(5)	0.7362(5)	0.3000(6)	0.6984(4)	1.9
C(6)	0.6712(5)	0.3555(6)	0.7389(4)	1.7
C(7)	0.7014(4)	0.4253(6)	0.8190(4)	1.5
C(8)	0.7955(4)	0.4577(6)	0.8487(4)	1.4
C(9)	0.5710(5)	0.3629(8)	0.6910(5)	2.5
C(10)	0.5575(4)	0.4657(7)	0.6103(4)	1.8
C(11)	0.6364(4)	0.5648(7)	0.6218(4)	1.6
C(12)	0.6508(4)	0.6685(6)	0.6841(4)	1.6
C(13)	0.7421(4)	0.7006(6)	0.7228(4)	1.4
C(14)	0.8161(4)	0.6524(6)	0.6918(4)	1.3
C(15)	0.7938(4)	0.5971(6)	0.6073(4)	1.5
C(16)	0.7063(4)	0.5399(6)	0.5788(4)	1.6
C(17)	0.8542(5)	0.6128(7)	0.5426(4)	2.0
C(18)	0.8525(5)	0.7641(7)	0.5088(5)	2.2
C(19)	0.7663(5)	0.8399(7)	0.5148(4)	1.9
C(20)	0.6793(5)	0.8027(6)	0.4656(4)	1.9
C(21)	0.6016(5)	0.8307(7)	0.4960(4)	2.0
C(22)	0.6082(5)	0.8956(7)	0.5757(4)	1.9
C(23)	0.6914(5)	0.9582(7)	0.6141(5)	2.0
C(24)	0.7703(5)	0.9306(6)	0.5844(4)	1.7
C(25)	0.5389(5)	0.8668(8)	0.6296(5)	2.4
C(26)	0.5742(5)	0.7517(7)	0.7030(4)	2.0
C(27)	0.8487(5)	0.2371(6)	0.9580(4)	1.7
C(28)	0.8495(4)	0.0820(6)	0.8252(4)	1.5
C(29)	0.6947(4)	0.1333(6)	0.8578(4)	1.7

Table 2. (Continued 2)

Molecule 2

Atom	x	y	z	B_{eq}/Å^2
Cr	0.19516(6)	0.72992(9)	0.66257(6)	1.03
O(1)	0.1166(5)	0.7408(5)	0.4653(3)	3.4
O(2)	0.0833(4)	0.4826(5)	0.6658(4)	2.7
O(3)	0.3482(4)	0.5395(6)	0.6519(4)	3.1
C(1)	0.0655(4)	1.1573(6)	0.7306(4)	1.7
C(2)	0.0403(4)	1.0195(7)	0.6792(4)	1.8
C(3)	0.1233(4)	0.9266(6)	0.6962(4)	1.4
C(4)	0.1405(4)	0.8317(6)	0.7656(4)	1.4
C(5)	0.2300(5)	0.7857(7)	0.8050(4)	1.8
C(6)	0.3040(4)	0.8340(6)	0.7743(4)	1.7
C(7)	0.2848(4)	0.9061(6)	0.6938(4)	1.7
C(8)	0.1958(4)	0.9506(6)	0.6549(4)	1.4
C(9)	0.4003(5)	0.8274(8)	0.8342(5)	2.8
C(10)	0.4122(4)	0.9481(7)	0.9016(4)	2.0
C(11)	0.3333(4)	1.0491(6)	0.8796(4)	1.5
C(12)	0.3258(4)	1.1537(6)	0.8174(4)	1.6
C(13)	0.2374(4)	1.1934(6)	0.7714(4)	1.4
C(14)	0.1582(4)	1.1517(6)	0.7965(4)	1.4
C(15)	0.1732(4)	1.0924(6)	0.8818(4)	1.5
C(16)	0.2576(4)	1.0326(6)	0.9154(4)	1.5
C(17)	0.1069(4)	1.1127(7)	0.9397(4)	1.8
C(18)	0.1129(5)	1.2578(7)	0.9788(4)	2.0
C(19)	0.2042(5)	1.3261(7)	0.9794(4)	1.8
C(20)	0.2863(5)	1.2747(7)	1.0339(4)	2.1
C(21)	0.3687(5)	1.2949(7)	1.0106(4)	2.2
C(22)	0.3721(5)	1.3643(7)	0.9342(4)	2.0
C(23)	0.2933(5)	1.4399(7)	0.8904(5)	2.1
C(24)	0.2095(4)	1.4209(7)	0.9141(4)	1.9
C(25)	0.4450(5)	1.3328(7)	0.8862(5)	2.3
C(26)	0.4074(4)	1.2339(7)	0.8063(5)	1.9
C(27)	0.1478(5)	0.7359(7)	0.5418(5)	2.2
C(28)	0.1260(4)	0.5793(6)	0.6669(4)	1.5
C(29)	0.2888(4)	0.6142(7)	0.6537(4)	1.8

used at the final stage of the refinement were: a=0.0767 and b=0.0005 for the monoclinic form and a=0.2271 and b=0.0032 for the triclinic form. The final atomic parameters of both forms are listed in Table 2.††††

The atomic scattering factors for the Cr, O, and C atoms were taken from the International Tables for X-Ray Crystallography, Vol. IV,[8] and those for H atom, from Stewart, Davidson, and Simpson.[9] Calculations were done on an ACOS 900 computer (Computation Center) and, at the final stage, on an ACOS 850 computer, (Crystallographic Research Center, Institute for Protein Research), Osaka University.

††††Tables of the anisotropic temperature factors, the coordinates of the hydrogen atoms, and the observed and calculated structure factors are kept at the Chemical Society of Japan, Document No. 8735.

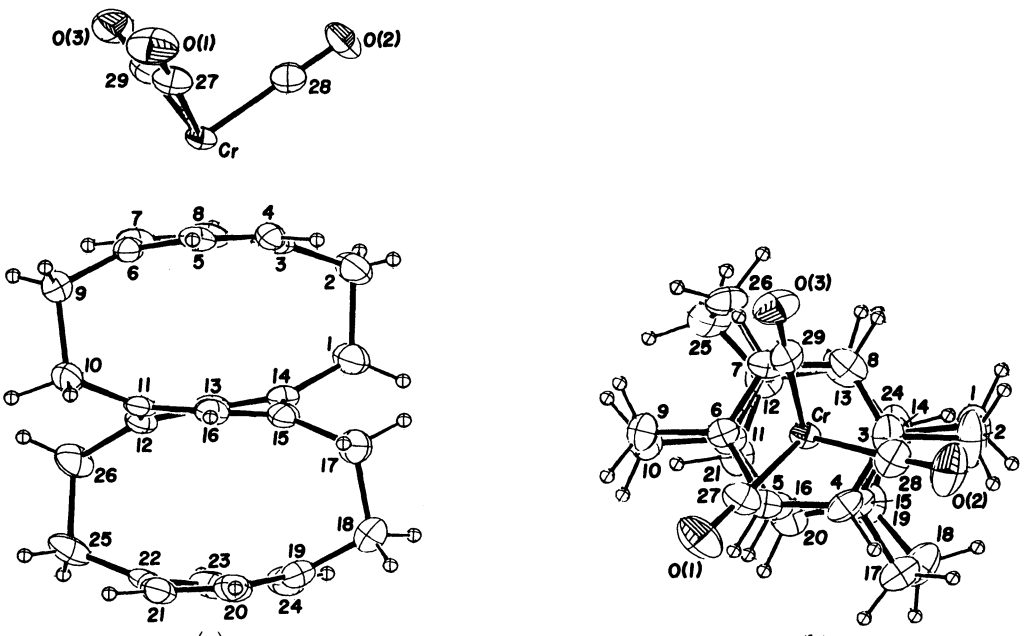


Fig. 1. A perspective view[10] of the molecule, together with the numbering scheme of the nonhydrogen atoms. Nonhydrogen atoms are drawn as thermal ellipsoids with 30% probability level, and the hydrogen atoms as spheres with B=1.0Å^2. a) Projected down from the C(16) to C(13) atoms in the middle layer benzene ring, b) projected onto the base plane of the upper layer benzene.

Table 3. Interatomic Bond Distances and Angles in Tricarbonyl(triple-layered [2.2]paracyclophane)-chromium, together, with the Estimated Standard Deviations in Parentheses

Bond distance/Å

	Monoclinic form (−95 °C)	Triclinic form (−160 °C) Molecule 1	Triclinic form (−160 °C) Molecule 2
Cr -C(27)	1.839(5)	1.847(6)	1.846(7)
Cr -C(28)	1.841(5)	1.846(6)	1.839(6)
Cr -C(29)	1.832(4)	1.824(6)	1.839(6)
O(1) -C(27)	1.159(7)	1.159(8)	1.172(9)
O(2) -C(28)	1.158(6)	1.151(7)	1.157(7)
O(3) -C(29)	1.160(6)	1.179(8)	1.161(8)
C(1) -C(2)	1.586(8)	1.576(9)	1.593(9)
C(1) -C(14)	1.521(6)	1.529(8)	1.513(8)
C(2) -C(3)	1.509(7)	1.531(8)	1.511(8)
C(3) -C(4)	1.413(6)	1.399(8)	1.403(8)
C(3) -C(8)	1.415(7)	1.415(8)	1.420(8)
C(4) -C(5)	1.385(6)	1.410(9)	1.401(8)
C(5) -C(6)	1.421(6)	1.402(9)	1.405(9)
C(6) -C(7)	1.405(6)	1.413(8)	1.406(8)
C(6) -C(9)	1.502(6)	1.506(10)	1.516(9)
C(7) -C(8)	1.388(7)	1.415(8)	1.389(8)
C(9) -C(10)	1.591(7)	1.587(9)	1.585(10)
C(10)-C(11)	1.516(6)	1.525(8)	1.514(9)
C(11)-C(12)	1.417(6)	1.406(8)	1.400(8)
C(11)-C(16)	1.397(6)	1.404(8)	1.400(8)
C(12)-C(13)	1.386(6)	1.397(8)	1.394(8)
C(12)-C(26)	1.520(7)	1.499(9)	1.514(9)
C(13)-C(14)	1.405(6)	1.403(8)	1.409(8)
C(14)-C(15)	1.408(6)	1.400(8)	1.418(8)
C(15)-C(16)	1.395(6)	1.407(8)	1.373(8)
C(15)-C(17)	1.525(7)	1.529(9)	1.519(9)
C(17)-C(18)	1.580(8)	1.583(9)	1.563(9)
C(18)-C(19)	1.518(7)	1.514(9)	1.536(9)
C(19)-C(20)	1.396(7)	1.397(9)	1.399(9)
C(19)-C(24)	1.393(7)	1.411(9)	1.400(9)
C(20)-C(21)	1.387(7)	1.395(9)	1.394(9)
C(21)-C(22)	1.411(7)	1.393(9)	1.386(9)
C(22)-C(23)	1.387(7)	1.400(9)	1.414(9)
C(22)-C(25)	1.520(7)	1.523(9)	1.509(9)
C(23)-C(24)	1.374(7)	1.403(9)	1.414(9)
C(25)-C(26)	1.579(8)	1.600(10)	1.590(9)

Table 3. (Continued)

Bond distance/Å			
Cr -C(3)	2.329(5)	2.330(5)	2.347(6)
Cr -C(4)	2.205(5)	2.219(6)	2.232(6)
Cr -C(5)	2.191(5)	2.234(7)	2.236(6)
Cr -C(6)	2.347(4)	2.335(6)	2.333(6)
Cr -C(7)	2.245(5)	2.223(6)	2.201(6)
Cr -C(8)	2.228(5)	2.183(6)	2.190(6)
Bond angle/°			
C(27)-Cr -C(28)	92.8(3)	89.6(3)	88.6(3)
C(27)-Cr -C(29)	88.8(3)	93.5(3)	92.3(3)
C(28)-Cr -C(29)	87.7(3)	88.1(3)	87.1(3)
Cr -C(27)-O(1)	177.7(5)	177.5(6)	179.0(7)
Cr -C(28)-O(2)	177.4(5)	179.0(6)	176.7(6)
Cr -C(29)-O(3)	178.3(4)	176.5(6)	177.0(6)
C(2) -C(1) -C(14)	111.7(4)	113.9(5)	112.9(5)
C(1) -C(2) -C(3)	110.1(4)	109.9(5)	110.4(5)
C(2) -C(3) -C(4)	120.1(5)	120.5(6)	121.1(6)
C(2) -C(3) -C(8)	121.0(5)	120.4(5)	120.8(5)
C(4) -C(3) -C(8)	118.1(5)	117.6(6)	116.9(6)
C(3) -C(4) -C(5)	120.2(5)	121.0(6)	121.1(6)
C(4) -C(5) -C(6)	120.8(4)	119.6(6)	119.8(6)
C(5) -C(6) -C(7)	117.2(4)	119.4(6)	118.5(6)
C(5) -C(6) -C(9)	120.5(4)	120.8(6)	119.6(6)
C(7) -C(6) -C(9)	120.9(4)	119.0(6)	121.2(6)
C(6) -C(9) -C(10)	110.7(4)	109.2(6)	108.9(6)
C(9) -C(10)-C(11)	112.7(4)	112.3(6)	113.1(6)
C(10)-C(11)-C(16)	121.0(4)	118.9(6)	120.0(6)
C(12)-C(11)-C(16)	116.2(4)	117.2(6)	115.8(6)
C(11)-C(12)-C(13)	116.4(4)	116.4(6)	117.1(6)
C(11)-C(12)-C(26)	123.0(4)	123.2(6)	122.9(5)
C(13)-C(12)-C(26)	119.8(4)	120.2(6)	119.6(6)
C(12)-C(13)-C(14)	123.4(5)	123.2(6)	122.6(6)
C(1) -C(14)-C(13)	119.5(4)	120.8(5)	120.2(6)
C(1) -C(14)-C(15)	124.0(4)	123.0(6)	123.5(6)
C(14)-C(15)-C(16)	116.7(4)	116.9(6)	116.3(6)
C(14)-C(15)-C(17)	123.3(4)	122.9(6)	122.5(6)
C(16)-C(15)-C(17)	119.7(4)	119.7(6)	120.5(6)
C(11)-C(16)-C(15)	123.2(5)	121.9(6)	124.2(6)
C(15)-C(17)-C(18)	112.6(5)	110.8(6)	111.9(6)
C(17)-C(18)-C(19)	111.6(5)	112.4(6)	112.5(6)
C(18)-C(19)-C(20)	121.3(5)	121.8(6)	119.8(6)
C(18)-C(19)-C(24)	120.6(5)	119.5(6)	120.6(6)
C(20)-C(19)-C(24)	116.4(5)	117.3(6)	118.3(6)
C(19)-C(20)-C(21)	120.9(5)	120.4(6)	119.6(6)
C(20)-C(21)-C(22)	120.4(5)	121.4(6)	121.8(6)
C(21)-C(22)-C(23)	116.7(5)	117.1(6)	117.6(6)
C(21)-C(22)-C(25)	119.2(5)	120.2(6)	121.3(6)
C(23)-C(22)-C(25)	122.5(5)	120.7(6)	119.2(6)
C(22)-C(23)-C(24)	121.1(5)	120.7(6)	119.6(6)
C(19)-C(24)-C(23)	121.5(5)	120.2(6)	120.2(6)
C(22)-C(25)-C(26)	112.7(5)	112.4(6)	111.1(6)
C(12)-C(26)-C(25)	111.2(5)	111.9(6)	112.6(6)

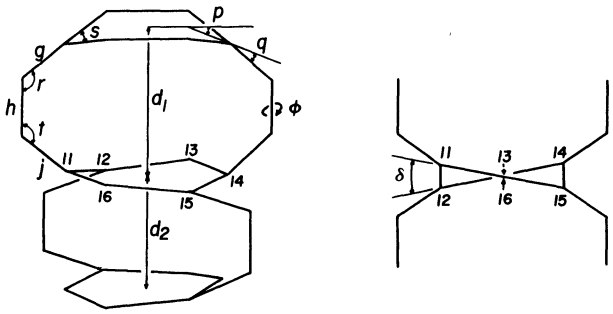
Results and Discussion

Molecular Structure. A perspective view (*ORTEP* drawing[10]) of the TC3PC molecule of the monoclinic form is shown in Fig. 1, along with the numbering scheme of the atoms. The interatomic bond distances and angles in the monoclinic-form and triclinic-form molecules are given in Table 3. Other important structural parameters of the cyclophane skeleton in the three TC3PC molecules are compared in Table 4 with those of BR3PC and TCPC. No essential difference is found between the structures of the one monoclinic-form molecule and the two triclinic-form molecules. Therefore, the discussion hereafter will be done on the molecular structure of the monoclinic form unless otherwise stated.

Some remarkable features of the triple-layered [2.2]paracyclophane moiety are observed. Both the upper- and lower-layer benzene rings take the boat form. This fact is commonly observed for the outermost benzene rings of multiple-layered [2.2]paracyclophanes. The upper-layer benzene ring in the present complex is less deformed from the plane than that of the lower layer benzene ($p+q<p'+q'$ in Table 4). On the other hand, the second layer benzene ring is twisted along the line passing through the C(13) and C(16) atoms, which are not linked by $-CH_2-CH_2-$ bridges; the twist angle is 13.4°, which is equal to that [13.4°] in tetramethyl quadruple-layered [2.2]paracyclophane.[11]

Table 4. Mean Molecular Structures of TC3PC and Related Compounds

	TC3PC			BR3PC[4]	TCPC[1]
	Monoclinic form (−95°C)	Triclinic form (−160°C) Molecule 1	Molecule 2		
Upper-layer benzene ring					
p/°	11.0	11.3	11.4	12.1	12.2
q/°	10.3	10.5	9.7	11.4	8.9
s/°	117.7	118.5	117.7	117.2	118.3
$-CH_2-CH_2-$ bridge between upper- and middle-layer benzene rings					
g/Å	1.506	1.519	1.514	1.513	1.510
h/Å	1.589	1.582	1.589	1.580	1.595
j/Å	1.519	1.527	1.514	1.515	
r/°	110.4	109.6	109.7	112.4	110.9
t/°	112.2	113.1	113.0	112.0	112.8
ϕ/°	11.5	17.4	10.4	15.1	3.8
Middle-layer benzene ring					
δ/°	13.4	13.6	13.5	13.6	
$-CH_2-CH_2-$ bridge between middle- and lower-layer benzene rings					
g'/Å	1.519	1.519	1.523		1.519
h'/Å	1.580	1.592	1.577		
j'/Å	1.523	1.514	1.517		
r'/°	112.2	112.4	111.8		
t'/°	111.9	111.4	112.3		
ϕ'/°	21.9	21.4	21.7		
Lower-layer benzene ring					
p'/°	11.8	11.8	11.9		11.4
q'/°	12.5	12.8	9.5		11.2
s'/°	116.6	117.2	118.0		116.9
Interring distances between upper and middle (d_1) and between middle and lower benzenes (d_2)					
d_1/Å	2.979	3.004	2.989	3.046	
d_2/Å	3.057	3.053	3.049	3.046	



The C-C distances of the $-CH_2-CH_2-$ bridges are 1.591(7) and 1.586(8) Å (from the upper layer to the middle) and 1.579(8) and 1.580(8) Å (from the middle layer to the lower), values which are comparable to those of TCPC [1.591(7) and 1.599(8) Å] and much longer than the usual C-C single bond. The torsional angles around the $-CH_2-CH_2-$ bond between the upper and middle layers [13.2 and 9.7°] are much smaller than those between the middle and lower layers [20.1 and 23.6°]. As may be seen in Fig. 1(b), the three benzene rings are not in the eclipsed position; they are mutually rotated slightly in a helical way, similar to those in BR3PC and inner triple-layered paracyclophanequinone.[12]

The $Cr(CO)_3$ group in tricarbonyl(benzene)chromium (TCB)[13] takes the staggered configuration to the benzene ring because of the crystallographic mirror symmetry of the molecule, each of the three Cr-C≡O branches projected is perpendicular to the C-C bond of the benzene ring. The C-C bond distances in the benzene ring show a bond alternation. The $Cr(CO)_3$ in TCPC shows a slight deviation from the staggered position. The mean angular deviation (θ_{av}) of a Cr-C≡O branch from the staggered configuration is 3.6° in TCPC, while the remainder of the bond alternation can be seen in the upper-layer benzene ring. In the present complex, the relative positions of the $Cr(CO)_3$ group projected onto the upper-layer benzene

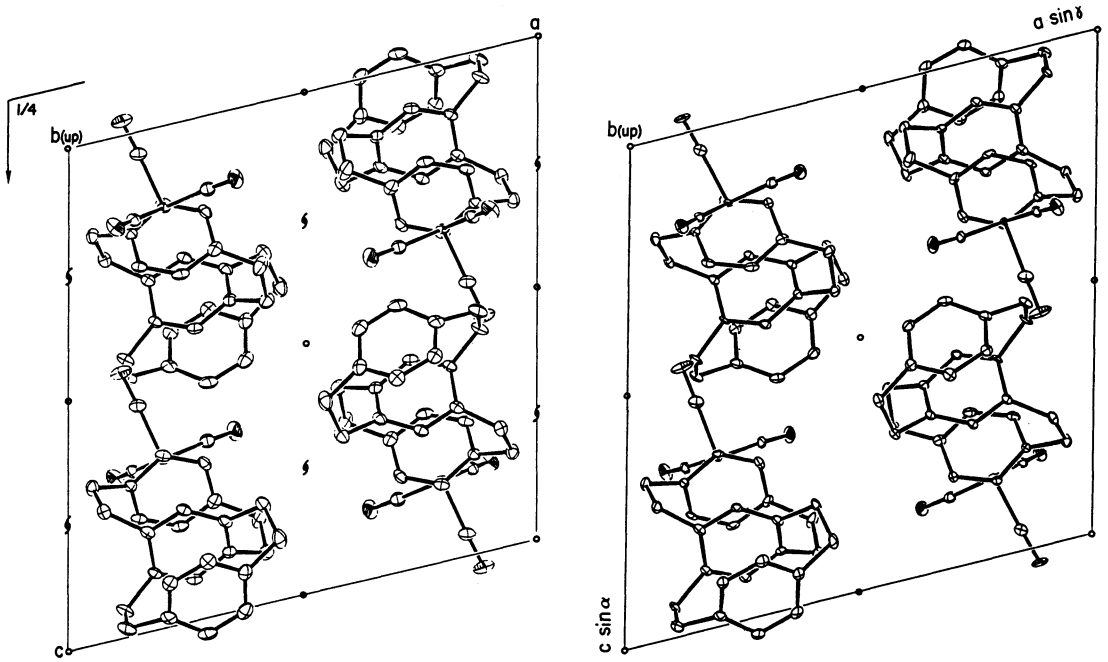


Fig. 2. Crystal structure projected along the b axis.[10] a) Monoclinic form, b) Triclinic form.

ring in the monoclinic- (θ_{av}: 15.6°) and triclinic-form (θ_{av}: 18.9 and 18.4°) molecules are in between the staggered and eclipsed configurations. No bond alternation is observed in the upper-layer benzene rings in these complexes.

The interlayer distances from the base planes of the boat-shaped upper- and lower-layer benzene rings to the least-squares plane of middle-layer twisted benzene are compared with those in BR3PC in Table 4. In TC3PC, the d_1 distance between the upper- and middle-layer benzene rings is significantly shorter than the d_2 distance between the middle- and lower-layer benzenes. The d_2 distances are essentially equal to that in BR3PC. The shortening of the d_1 compared with d_2 results from the strong electron-withdrawing effect of the $Cr(CO)_3$ group coordinated to the upper-layer benzene. However, the electronic effect of the $Cr(CO)_3$ group may not account for the shortening of d_2. The shortening of the interlayer distance by the coordination of the $Cr(CO)_3$ group to the benzene has also been found in the crystal structure of TCPC.

Crystal Structure. The packing of the molecules in the monoclinic- and triclinic-form crystals are shown in Fig. 2. The corresponding space group of the crystal changed from $P2_1/c$ to $P\bar{1}$ upon cooling. A slight difference is observed between the crystals of the two forms in their unit-cell dimensions (0.38% in a, 0.37% in b, and 0.13% in c; Table 1). Intermolecular contacts shorter than 3.5 Å were found between an oxygen atom of the $Cr(CO)_3$ moiety and a carbon atom of the upper-layer benzene ring or that of a $-CH_2-CH_2-$ bridge; in a monoclinic crystal: C(7)(x, y, z)$\cdots$O(1)(x, 0.5$-y$, $-0.5+z$)=3.416(6) Å, in a triclinic crystal: C(1^{ii})(x, y, z)$\cdots$O(2^{ii})(x, $1+y$, z)=3.404(8) Å, C(4^{i})(x, y, z)$\cdots$O(1^{ii})-($1-x$, $1-y$, $1-z$)=3.420(9) Å, and C(2^{i})(x, y, z)$\cdots$O(2^{ii})($1+x$, y, z)=3.383(8) Å, where the superscripts i and ii show the two independent molecules.

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