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Implications of X-Ray Crystallographic Results of 1,2,3,4-Tetrachloro-9-(2-oxopropyl)triptycene Rotamers

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Crystals of 1,2,3,4-tetrachloro-9-(2-oxopropyl)triptycene grown from tetrahydrofuran-hexane were found to contain 1:1 *ap* and ±*sc* rotational isomers about the C_9–C_{Pr} bond by the X-ray diffraction method. The molecular structures had the following features. The acetyl group in the 9-substituent takes an *O*-inside, relative to the triptycene skeleton, conformation in both forms. The benzene rings are deformed by the steric effect to form boats. The 2-oxopropyl groups in both forms were planar within the experimental error but the C_2–C_1 bond in the 2-oxopropyl group was appreciably shorter in the ±*sc* conformation than that in the *ap*. The results are discussed on the ground of steric repulsion and the existence of the interaction between the C=O and the Cl groups which are located only 3.035 Å apart in the ±*sc* form.

A number of 9-substituted triptycenes was synthesized to manifest isolation of stable rotational isomers and to examine the effects of substituents on the rotational barrier.[2,3] Out of these studies, it has emerged that triptycenes which carry a *t*-alkyl group in the 9-position exhibited high enough barriers to rotation to isolate the rotamers at room temperature, whereas those carrying an *s*-alkyl group in the 9-position possess barriers to rotation which are borderline values for isolation of rotamers at room temperature.

Triptycenes carrying a primary 9-substituent exhibit still lower barriers than 9-*s*-alkyltriptycenes and the internal rotation in 9-(primary alkyl)triptycenes is frozen only on the NMR time scale at low temperatures which are easily accessible. Although the internal rotation is fast in these compounds, the population ratios of the rotamers concerned afford interesting information. Since the peri-substituent in the 1-position of the triptycene skeleton is very closely located to the second atom of the 9-substituent, if a proper rotational form is taken, a weak interaction, which is not otherwise detected, can be detected as a change in populations of rotamers due to the highly congested state.

We found that unusually facile cyclization occurs, if a cationoid is formed in the second atom of the 9-substituent, between the cationoid center and the 1-methoxyl group in 9-substituted 1,4-dimethoxytriptycenes.[4] 9-(2-Acyloxyethyl)-1,4-dimethoxytriptycenes show higher ±*sc*/*ap* values when the acyl group becomes more electronegative to indicate that an interaction exists between the acyloxymethyl and the 1-methoxyl groups.[5] 9-Substituted triptycenes carrying a carbonyl group in the 2-position of the 9-substituent showed high ±*sc*/*ap* values, if there is an electron-donating substituent in the 1-position of triptycene, to suggest that there is an attractive interaction between the carbonyl and the 1-substituent.[6] All of these results imply that the triptycene system is a good model to find a weak, often hidden interaction by either a reaction or population distribution.

During the course of investigation on *n*-donor-carbonyl interaction, we encountered a queer phenomenon. Apparently a formyl group is less electron accepting than an acetyl group. This is contrary to the common sense of organic chemistry because aldehydes are usually more reactive than ketones toward nucleophiles. We suspected that the origin of this anomaly might be the presence of different conformations in aldehydes from those of ketones. Since a hydrogen is much smaller than an oxygen atom in a formyl group, an oxygen-inside conformation relative to the triptycene skeleton is of prohibitively high energy in the case of 9-(2-oxoethyl)triptycenes, while such a conformation will be favored in the case of 9-(2-oxopropyl)triptycenes because an oxygen atom is smaller than a methyl group. Unfortunately, strongly interacting formyl compounds did not give crystals suitable for X-ray analysis. However, 1,4-dimethyl-9-(2-oxoethyl)triptycene gave good crystals and its *ap* form was shown by X-ray crystallography to exist as an oxygen-outside conformation.[6b]

1,2,3,4-Tetrachloro-9-(2-oxopropyl)triptycene, which was known to exist as ±*sc* conformations solely in solution,[6] was found to give good crystals in which both ±*sc* and *ap* conformations are contained. Thus fortunately we can now compare the molecular structures of ±*sc* and *ap* forms of this compound. This paper reports the outcome of the investigation and discusses the implications of the results.

Experimental

Crystals of 1,2,3,4-tetrachloro-9-(2-oxopropyl)triptycene was grown from a tetrahydrofuran-hexane solution. A crystal with dimensions $0.45 \times 0.44 \times 0.37$ mm^3 was mounted on a Rigaku automated four-circle diffractometer and the intensity data were collected using Mo *K*α radiation monochromated by a graphite plate. The θ-2θ scan technique was employed to collect the intensities with $|F_o| \geq 3\sigma|F_o|$ in the range $2\theta \leq 57°$. A total of 6067 reflections were used for analysis.

The crystal data are as follows: $C_{23}H_{14}Cl_4O$, F.W.=448.18, monoclinic, space group $P2_1/a$, a=30.812(2) Å, b=8.304(1) Å, c=15.103(1) Å, β=97.19(1)°, Z=8, D_x=1.55 g cm^{-3}, μ(Mo $K\alpha$)=6.29 cm^{-1}.

The structure was solved by the direct method. Isotropic temperature factors were used for hydrogen atoms and anisotropic temperature factors were employed for others. All these positional and thermal parameters were refined by the least-squares method including the anomalous scattering corrections for chlorine, oxygen, and carbon atoms. The atomic scattering factors were taken from a literature.[7] The final R value was 0.048.

Table 1. Atomic posisional parameters ($\times 10^4$) with estimated standard deviations in parentheses and anisotropic temperature factors ($\times 10^4$)[a)]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
$\pm$*sc* Form									
Cl$_1$	2227(0)	2324(1)	2792(0)	9(0)	234(2)	41(0)	−3(0)	−2(0)	−5(0)
Cl$_2$	1938(0)	355(1)	4312(0)	16(0)	235(2)	29(0)	16(0)	−2(0)	5(0)
Cl$_3$	982(0)	−768(1)	4277(0)	20(0)	192(1)	35(0)	−1(0)	10(0)	16(0)
Cl$_4$	305(0)	−90(1)	2603(0)	11(0)	233(2)	52(0)	−12(0)	10(0)	5(0)
C$_1$	1700(1)	1545(4)	2647(1)	8(0)	120(5)	31(1)	5(1)	0(0)	−6(2)
C$_2$	1567(1)	724(4)	3379(1)	11(0)	131(5)	24(1)	10(1)	0(0)	−4(2)
C$_3$	1143(1)	197(4)	3368(1)	13(0)	110(5)	27(1)	3(1)	6(0)	0(2)
C$_4$	844(1)	512(4)	2616(1)	9(0)	130(5)	33(1)	0(1)	6(0)	−3(2)
C$_5$	605(1)	144(4)	−363(2)	8(0)	155(6)	34(1)	−3(1)	1(0)	0(2)
C$_6$	805(1)	−426(4)	−1071(2)	12(0)	146(6)	28(1)	0(1)	0(0)	−9(2)
C$_7$	1231(1)	−32(4)	−1134(1)	12(0)	150(6)	23(1)	9(1)	2(0)	0(2)
C$_8$	1466(1)	945(4)	−501(1)	8(0)	134(5)	28(1)	3(1)	4(0)	6(2)
C$_9$	1479(0)	2609(3)	975(1)	6(0)	100(4)	27(1)	2(1)	2(0)	1(1)
C$_{10}$	665(1)	1836(4)	1078(1)	6(0)	165(6)	29(1)	0(1)	2(0)	3(2)
C$_{11}$	733(1)	3637(4)	1014(1)	9(0)	145(5)	23(1)	9(1)	1(0)	1(2)
C$_{12}$	412(1)	4808(5)	1007(2)	10(0)	222(8)	33(1)	18(1)	2(0)	0(2)
C$_{13}$	528(1)	6402(5)	958(2)	18(0)	182(7)	46(1)	32(1)	2(0)	3(3)
C$_{14}$	952(1)	6829(4)	917(2)	20(0)	110(5)	44(1)	15(1)	0(0)	−5(2)
C$_{15}$	1276(1)	5668(4)	913(2)	12(0)	118(5)	33(1)	3(1)	0(0)	−2(2)
C$_{16}$	1165(1)	4067(4)	960(1)	9(0)	114(5)	22(1)	7(1)	1(0)	0(1)
C$_{17}$	1411(1)	1771(3)	1875(1)	7(0)	92(4)	26(1)	4(1)	3(0)	−3(1)
C$_{18}$	973(1)	1296(3)	1890(1)	7(0)	108(5)	27(1)	2(1)	3(0)	−3(2)
C$_{19}$	1270(1)	1491(3)	219(1)	8(0)	88(4)	26(1)	3(1)	2(0)	5(1)
C$_{20}$	838(1)	1097(4)	275(1)	8(0)	120(5)	27(1)	1(1)	2(0)	2(2)
C$_{21}$	1938(1)	3128(4)	824(2)	7(0)	109(5)	39(1)	0(1)	2(0)	6(2)
C$_{22}$	2286(1)	1868(4)	816(2)	8(0)	156(6)	38(1)	4(1)	2(0)	12(2)
C$_{23}$	2708(1)	2471(7)	566(4)	10(0)	322(13)	128(4)	13(2)	16(1)	77(6)
O	2232(0)	481(3)	1000(1)	12(0)	143(4)	50(1)	9(1)	4(0)	5(2)
ap Form									
Cl$_1$	1914(0)	4720(1)	4871(0)	11(0)	203(1)	43(0)	−4(0)	6(0)	28(0)
Cl$_2$	1223(0)	5336(1)	3282(0)	19(0)	193(1)	30(0)	10(0)	6(0)	23(0)
Cl$_3$	257(0)	4365(1)	3319(0)	17(0)	254(2)	34(0)	16(0)	−7(0)	8(0)
Cl$_4$	−20(0)	2643(1)	4985(0)	8(0)	235(2)	50(0)	−1(0)	−5(0)	−4(0)
C$_1$	1388(1)	4038(4)	4943(1)	9(0)	108(5)	28(1)	4(1)	3(0)	0(2)
C$_2$	1073(1)	4386(4)	4211(1)	14(0)	107(5)	22(1)	9(1)	3(0)	0(2)
C$_3$	642(1)	3965(4)	4219(1)	12(0)	125(5)	26(1)	11(1)	−3(0)	−5(2)
C$_4$	520(1)	3191(4)	4966(1)	8(0)	118(5)	31(1)	5(1)	−1(0)	−8(2)
C$_5$	839(1)	−1102(4)	6550(1)	10(0)	123(5)	28(1)	−6(1)	0(0)	−1(2)
C$_6$	1127(1)	−2372(4)	6531(2)	15(0)	96(5)	42(1)	−4(1)	0(0)	−1(2)
C$_7$	1563(1)	−2079(4)	6499(2)	14(0)	105(5)	43(1)	11(1)	0(0)	−4(2)
C$_8$	1726(1)	−515(4)	6504(1)	9(0)	123(5)	31(1)	7(1)	1(0)	4(2)
C$_9$	1557(0)	2578(3)	6546(1)	6(0)	99(4)	24(1)	3(1)	1(0)	5(1)
C$_{10}$	723(1)	1962(3)	6517(1)	6(0)	111(5)	30(1)	−1(1)	1(0)	3(2)
C$_{11}$	900(1)	3027(3)	7290(1)	7(0)	91(4)	23(1)	2(1)	1(0)	5(1)
C$_{12}$	654(1)	3656(4)	7916(1)	7(0)	130(5)	32(1)	3(1)	2(0)	6(2)
C$_{13}$	856(1)	4677(4)	8564(1)	9(0)	150(6)	30(1)	5(1)	3(0)	−9(2)
C$_{14}$	1290(1)	5059(4)	8574(1)	11(0)	127(5)	29(1)	0(1)	1(0)	−12(2)
C$_{15}$	1539(1)	4410(4)	7951(1)	7(0)	114(5)	30(1)	−1(1)	0(0)	1(2)
C$_{16}$	1341(0)	3376(3)	7307(1)	7(0)	86(4)	22(1)	2(0)	1(0)	3(1)
C$_{17}$	1270(1)	3219(3)	5679(1)	8(0)	85(4)	24(1)	3(1)	1(0)	−1(1)
C$_{18}$	827(1)	2829(3)	5684(1)	8(0)	90(4)	25(1)	3(1)	0(0)	−5(1)
C$_{19}$	1442(1)	760(3)	6543(1)	8(0)	102(4)	22(1)	1(1)	1(0)	1(1)
C$_{20}$	999(1)	447(3)	6553(1)	8(0)	97(4)	22(1)	−1(1)	0(0)	−3(1)
C$_{21}$	2047(1)	2862(4)	6624(1)	7(0)	117(5)	32(1)	0(1)	3(0)	8(2)
C$_{22}$	2323(1)	2163(4)	7451(2)	8(0)	122(5)	34(1)	2(1)	1(0)	−1(2)
C$_{23}$	2805(1)	2399(5)	7458(2)	7(0)	242(9)	59(2)	1(1)	−1(0)	33(3)
O	2176(0)	1492(3)	8045(1)	10(0)	220(5)	37(1)	0(1)	1(0)	30(2)

a) The form of the anisotropic temperature factor is: $T=\exp(-B_{11}h^2-B_{22}k^2-B_{33}l^2-2B_{12}hk-2B_{13}hl-2B_{23}kl)$.

Results and Discussion

The nonhydrogen atomic positional parameters are tabulated in Table 1. In the crystalline state, two molecules, *ap* and +(or −)*sc*, coexist in an asymmetric unit, as shown in Fig. 1. The coexistence of *ap* and ±*sc* conformations enables us to compare the structural features and to discuss the implications of the structures which were not possible in other triptycenes.

We point out first that the acetyl groups in both conformations take the *O*-inside conformation, as are seen in Fig. 1. Thus the difference in conformations about the carbonyl moieties in the formyl and the acetyl compounds is now verified. The Coulombic attraction between the acetyl group and the peri-chloro must be playing some role in stabilizing the ±*sc* form

Table 2. Bond lengths and bond angles in 1,2,3,4-tetrachloro-9-(2-oxopropyl)triptycene

Bond length	l/Å		Bond length	l/Å	
	±*sc*	*ap*		±*sc*	*ap*
C_1-Cl_1	1.736(3)	1.735(4)	C_9-C_{19}	1.548(4)	1.551(4)
C_1-C_2	1.403(5)	1.407(4)	C_9-C_{21}	1.521(4)	1.519(4)
C_1-C_{17}	1.389(4)	1.389(4)	C_{10}-C_{11}	1.515(5)	1.512(4)
C_2-Cl_2	1.728(3)	1.722(3)	C_{10}-C_{18}	1.521(4)	1.519(4)
C_2-C_3	1.374(5)	1.375(5)	C_{10}-C_{20}	1.515(5)	1.516(4)
C_3-Cl_3	1.717(3)	1.721(3)	C_{11}-C_{12}	1.385(5)	1.385(4)
C_3-C_4	1.396(4)	1.389(5)	C_{11}-C_{16}	1.390(5)	1.387(4)
C_4-Cl_4	1.732(4)	1.732(4)	C_{12}-C_{13}	1.375(6)	1.383(5)
C_4-C_{18}	1.377(5)	1.379(4)	C_{13}-C_{14}	1.361(7)	1.371(5)
C_5-C_6	1.382(5)	1.381(5)	C_{14}-C_{15}	1.388(6)	1.395(5)
C_5-C_{20}	1.378(4)	1.377(5)	C_{15}-C_{16}	1.377(5)	1.381(4)
C_6-C_7	1.370(5)	1.372(6)	C_{17}-C_{18}	1.408(4)	1.405(4)
C_7-C_8	1.387(4)	1.392(5)	C_{19}-C_{20}	1.383(4)	1.392(5)
C_8-C_{19}	1.385(4)	1.381(5)	C_{21}-C_{22}	1.499(5)	1.535(4)
C_9-C_{16}	1.550(4)	1.547(4)	C_{22}-C_{23}	1.487(6)	1.496(5)
C_9-C_{17}	1.564(4)	1.578(4)	C_{22}-O	1.201(5)	1.192(4)

Bond angle	ϕ/°		Bond angle	ϕ/°	
	±*sc*	*ap*		±*sc*	*ap*
Cl_1-C_1-C_2	116.3(2)	116.2(3)	C_{10}-C_{11}-C_{16}	113.5(3)	113.3(3)
Cl_1-C_1-C_{17}	123.1(2)	123.4(2)	C_{12}-C_{11}-C_{16}	120.4(4)	121.8(3)
C_2-C_1-C_{17}	120.5(3)	120.4(3)	C_{11}-C_{12}-C_{13}	119.1(4)	118.4(3)
Cl_2-C_2-C_1	119.9(3)	120.4(3)	C_{12}-C_{13}-C_{14}	120.6(4)	120.1(3)
Cl_2-C_2-C_3	119.0(3)	118.8(3)	C_{13}-C_{14}-C_{15}	120.9(4)	121.4(3)
C_1-C_2-C_3	121.1(3)	120.8(3)	C_{14}-C_{15}-C_{16}	119.1(4)	118.8(4)
Cl_3-C_3-C_2	120.5(3)	121.0(3)	C_9-C_{16}-C_{11}	113.6(3)	114.1(2)
Cl_3-C_3-C_4	120.7(3)	120.1(3)	C_9-C_{16}-C_{15}	126.6(3)	126.6(3)
C_2-C_3-C_4	118.7(3)	118.9(3)	C_{11}-C_{16}-C_{15}	119.8(3)	119.3(3)
Cl_4-C_4-C_3	119.4(3)	119.5(2)	C_1-C_{17}-C_{18}	117.6(3)	118.0(3)
Cl_4-C_4-C_{18}	120.1(2)	119.8(3)	C_1-C_{17}-C_9	130.4(3)	130.9(3)
C_3-C_4-C_{18}	120.6(3)	120.8(3)	C_9-C_{17}-C_{18}	111.9(2)	111.2(2)
C_6-C_5-C_{20}	119.7(3)	119.0(3)	C_4-C_{18}-C_{10}	124.6(3)	124.0(3)
C_5-C_6-C_7	119.7(3)	120.0(3)	C_4-C_{18}-C_{17}	121.3(3)	121.1(3)
C_6-C_7-C_8	121.0(3)	121.3(4)	C_{10}-C_{18}-C_{17}	114.0(3)	114.9(3)
C_7-C_8-C_{19}	119.5(3)	119.1(3)	C_8-C_{19}-C_9	126.5(3)	126.9(3)
C_{16}-C_9-C_{17}	102.0(2)	103.0(2)	C_8-C_{19}-C_{20}	119.2(3)	119.1(3)
C_{16}-C_9-C_{19}	104.8(2)	107.4(2)	C_9-C_{19}-C_{20}	114.3(3)	114.0(3)
C_{16}-C_9-C_{21}	111.6(3)	113.1(2)	C_5-C_{20}-C_{10}	126.0(3)	125.3(3)
C_{17}-C_9-C_{19}	106.6(2)	102.8(2)	C_5-C_{20}-C_{19}	121.0(3)	121.6(3)
C_{17}-C_9-C_{21}	119.0(2)	117.4(2)	C_{10}-C_{20}-C_{19}	113.0(3)	113.0(3)
C_{19}-C_9-C_{21}	111.6(2)	112.1(3)	C_9-C_{21}-C_{22}	118.8(3)	116.7(3)
C_{11}-C_{10}-C_{18}	105.4(3)	105.6(3)	C_{21}-C_{22}-C_{23}	114.6(3)	113.8(3)
C_{11}-C_{10}-C_{20}	106.5(3)	108.1(2)	C_{21}-C_{22}-O	123.2(3)	124.4(3)
C_{18}-C_{10}-C_{20}	106.2(3)	104.3(3)	C_{23}-C_{22}-O	122.2(4)	121.8(3)
C_{10}-C_{11}-C_{12}	126.2(3)	124.9(3)			

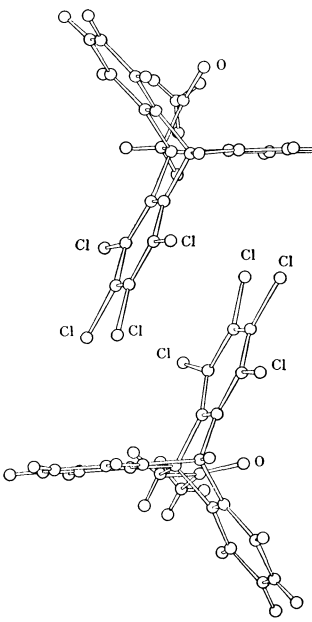

Fig. 1. A perspective drawing of 1,2,3,4-tetrachloro-9-(2-oxopropyl)triptycene.

Table 3. Atomic shifts from the least-squares planes

	A Ring d/Å			B Ring d/Å	
	±*sc*	*ap*		±*sc*	*ap*
C_1	−0.014	−0.027	C_5	−0.004	−0.008
C_2	0.002	−0.002	C_6	0.010	0.007
C_3	0.008	0.017	C_7	−0.005	0.006
C_4	−0.005	−0.008	C_8	−0.006	−0.010
C_{17}	0.016	0.034	C_{19}	0.012	0.010
C_{18}	−0.007	−0.013	C_{20}	−0.007	−0.004
	C Ring d/Å			2-Oxopropyl d/Å	
	±*sc*	*ap*		±*sc*	*ap*
C_{11}	−0.009	−0.006	C_{21}	0.000	0.000
C_{12}	0.001	0.003	C_{22}	0.001	−0.002
C_{13}	0.008	0.003	C_{23}	0.000	0.000
C_{14}	−0.008	−0.006	O	0.000	−0.001
C_{15}	0.000	0.002			
C_{16}	0.008	0.004			

Table 4. Dihedral angles formed by least-squares planes

Planes	ϕ/°	
	ap	+*sc*
A-B	113.2	125.9
A-C	118.4	114.0
B-C	128.3	120.0
A-Oxopropyl	173.1	61.4
B-Oxopropyl	62.9	66.7
C-Oxopropyl	65.4	167.4

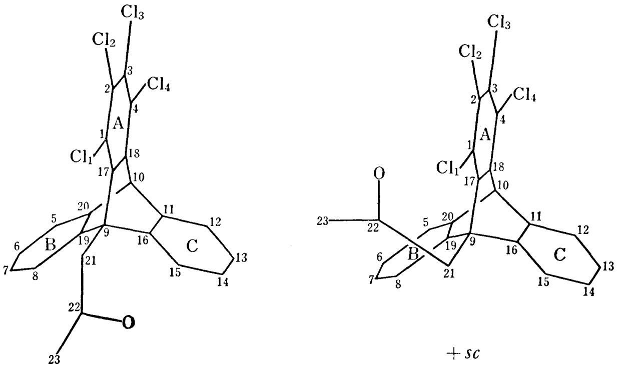

Fig. 2. Numberings of atoms and designations of rings in *ap*- and ±*sc*-1,2,3,4-tetrachloro-9-(2-oxopropyl)-triptycene.

of 1,2,3,4-tetrachloro-9-(2-oxopropyl)triptycene, in contrast to the Coulombic repulsion between the formyl and the peri-chloro groups in 1,2,3,4-tetrachloro-9-(2-oxoethyl)triptycene that should destabilize the ±*sc* form.

The intramolecular strain seems to be distributed widely over the molecules. This can be pointed out from bond lengths and bond angles (Table 2), atomic shifts from the least-squares planes of the carbon atoms in the aromatic groups (Table 3), and dihedral angles concerned (Table 4). Numberings of atoms and designations of rings are shown in Fig. 2.

There are some common features of structures in both *ap* and ±*sc* forms. The bond lengths of C_9–C_{17} are very large 1.578 Å in *ap* and 1.564 Å in ±*sc*, although these distances are not so long as that in 9-*t*-butyl-1,2,3,4-tetrachlorotriptycene.[8] Other bonds connecting the C_9 with the aromatic rings are also longer than the normal C_{sp^2}–C_{sp^3} bond and this point is apparent if one compares those with bonds connecting C_{10} with aromatic rings. The bond angles C_1–C_{17}–C_9 are extraordinarily large, reflecting the relief of steric strain by the deformation. The C_9–C_{21} bond lengths are shorter than normal C_{sp^3}–C_{sp^3} bonds: this is attributed to the increased s-character of the orbital concerned of C_9 because of the lengthening of other bonds involving C_9. The apex angle of the pyramid formed by C_9 with C_{16}, C_{17}, and C_{19} is smaller than that formed by C_{10} with C_{11}, C_{18}, and C_{20}, indicating that the steric repulsion between Cl_1 and the 9-substituent is relieved by this modification as well. The similar structural features were also found in 1,4-dimethyl-9-(2-oxoethyl)triptycene.[6b)]

The Cl_1–C_1 and C_9–C_{21} bonds are tilted against each other, as were the cases in 9-*t*-butyl-1,2,3,4-tetrachlorotriptycene.[8)] The bond angle deformation is much greater for the angle C_{17}–C_9–C_{21} than that for Cl_1–C_1–C_{17} because of the large force constant for the deformation of Cl–C_{sp^2}–C_{sp^2} and buttressing effect of the Cl_2 and others. The small apex angle of C_9 pyramid may also contribute to enlarging the angle C_{17}–C_9–C_{21}. Rather small difference in bond angles C_{17}–C_9–C_{21} between the *ap* and the ±*sc* forms may be taken as supportive in assuming that the ground state energies of the *ap* and the *sc* forms are nearly the same as far as the interaction between the 9-substituent and the flanking benzene rings are concerned. Relatively long C–Cl distances in both forms (average 1.728 Å) may be due to the repulsive force among chlorine atoms.

The least squares planes of aromatic rings were calculated from the positional parameters of carbon atoms comprising the rings. Dihedral angles made by two aromatic rings listed in Table 4 clearly demonstrate that the dihedral angles made by two benzene rings which flank the acetyl group are much larger than others in both *ap* and ±*sc* forms. This will mean that the carbonyl oxygen which extends into the gap between the two benzene rings interacts strongly with the aromatic rings.

Alternatively, the aromatic rings exhibit interesting features. Although less significant in another, the benzene rings flanking the acetyl group are distorted significantly. C_1 and C_8 in rings A and B which are close to the acetyl group are significantly displaced from what is expected from a molecular model to avoid repulsive interactions in the ±*sc* form. Similarly C_8 in the B ring and C_{15} in the C ring of the *ap* form show significant displacement. Examining the structures of these benzene rings, we notice that the carbon atoms para to each other are displaced from the least squares plane, which is made by other four carbons, to the same direction to form boats. They are C_3 and C_{17} in A, C_6 and C_{19} in B and C_{11} and C_{14} in C of the *ap* form, whereas C_3 and C_{17} in A, C_5 and C_8 in B and C_{11} and C_{14} in C of the ±*sc* isomer form also the bow and the stern of a boat. This makes a sharp contrast to the fact that triptycene itself possesses planar benzene rings within 0.01 Å.[9] There are a few examples of the boat form of twisted benzenes in the literature[10] and theoretical verification for the boat benzene was given.[11] However, the earlier works treat relatively small shifts from the mean plane and/or contain large ambiguities in atomic coordinates. Since the shift from the plane observed in this study is large and the standard deviations of the positional parameters perpendicular to the plane are small (*ca.* 0.003 Å) for carbon atoms, the results serve as unambiguous evidence for the stability of the boat form of benzene.

In contrast to the benzene rings, the 2-oxopropyl groups make perfect planes (Table 3), which nearly include the C_9–C_{10} axis. However, the planes of the 2-oxopropyl groups were not coplanar with the mean plane of the benzene ring which is *ap* to the group: the 2-oxopropyl group does not bisect the dihedral angle made by flanking benzene rings but are close to one of the two aromatic rings. The deviation from the anti-benzene planes are 6.9° (closer to ring B than to ring C) and 12.6° (closer to ring B than to ring A) for *ap* and ±*sc* forms respectively. It is reasonable to be so in the ±*sc* form because the steric repulsion between the ring A and the 2-oxopropyl group will be severe (for attractive interactions *vide infra*). The reason for the asymmetric structure of the *ap* form is not understood at the moment.

The structural features discussed so far are rather common for both conformations of 1,2,3,4-tetrachloro-9-(2-oxopropyl)triptycene but there are some structural features which are different when we go from the *ap* conformation to the ±*sc*. Bond lengths and bond angles, which show differences more than 3σ and 7σ, respectively, are listed in Table 5. The large bond angles of C_{17}–C_9–C_{19} for the ±*sc* form relative to the *ap* and the same trend of C_{16}–C_9–C_{19} for the *ap* form relative to the ±*sc* can be attributed to the steric effect of the 2-oxopropyl group, as were seen in the dihedral angles made by two aromatic rings. The large bond angle of C_{18}–C_{10}–C_{20} in the ±*sc* form, though smaller than 7σ, relative to the *ap* may have the same origin because the bond angle C_{11}–C_{10}–C_{20} is also larger in the *ap* form than in the ±*sc*.

Table 5. Structural parameters which differ by over the estimated errors on going from the ±*sc* to the *ap* isomers[a,b)]

Bond length	l/Å	Bond angle	ϕ/°
C_9–C_{17}	−0.014(4)	C_{16}–C_9–C_{19}	−2.6(2)
C_{21}–C_{22}	−0.036(5)	C_{17}–C_9–C_{19}	3.8(2)
		C_{17}–C_9–C_{21}	1.7(2)
		C_9–C_{21}–C_{22}	2.2(3)

a) The difference is shown in the form: parameter(*sc*)−parameter(*ap*). b) Those listed here show differences of $\Delta r \geq 3\sigma(r)$ and $\Delta\theta \geq 7\sigma(\theta)$.

The differences in other bond lengths and bond angles deserve further comment on the ground of the postulated Cl···C=O interaction.[5] We propose that the 2-oxopropyl group and its vicinity assume the structure of the *ap* conformation if there is no interaction which affects the structure. The *ap* form possesses the following features. The C_9–C_{17} bond is abnormally long for normal C_{sp^2}–C_{sp^3} bonds. This must be attributed to the steric effect of the 9-substituent. Another point of interest is the C_{21}–C_{22} bond: it is unusually long as a C_{sp^2}–C_{sp^3} bond. This together with the fact that the bond angle C_9–C_{21}–C_{22} is larger than the normal tetrahedral angle suggests that, to relieve the steric strain caused by the carbonyl oxygen and the flanking benzene rings, the 2-oxopropyl group is deformed.

Comparing the bond lengths of the ±*sc* and *ap* forms, one notices that the unusuality observed in the *ap* form is corrected to some extent: the C_9–C_{17} bond length and the C_{21}–C_{22} bond length become closer to the normal values in the ±*sc* form than in the *ap* form. However, the bond angles C_{17}–C_9–C_{21} and C_9–C_{21}–C_{22} are larger in the ±*sc* form than in the *ap* form. We wish to attribute the structural change to the relative positions of the 1-chloro and the carbonyl groups in space which are required for the Cl···C=O interaction, as suggested by Dunitz and his coworkers.[12] If the bonds are longer, the geometry is not favorable for the Cl···C=O interaction. Therefore the bonds must shrink from the values observed in the *ap* form in order to realize the interaction in the ±*sc* form. However, if the shrinkage occurred without change in bond angles, the steric repulsion between the carbonyl oxygen and the aromatic rings would be too great. Thus the molecule shrinks in the ±*sc* form at the expense of widening the bond angles for which energy required is small.

One might argue that if there is a Cl···C=O interaction, the nonplanarity of the 2-oxopropyl group should be observed as are the cases in N···C=O interactions.[12,13] However, we believe that the carbonyl

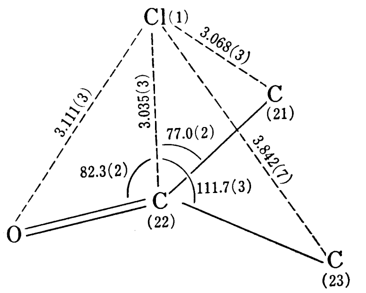

Fig. 3. Atomic distances and angles showing relative positions in space of the Cl_1 and the 2-oxopropyl group.

group in this case is under special conditions. As are depicted in Fig. 3, the Cl_1 atom located over the 2-oxopropyl group is over the C=O bond, closer to the carbon of the carbonyl group than the oxygen, to make $Cl_1 \cdots C_{22}$–O angle of 82.3° and is closer to the C_{21} atom than the C_{23}. Under the optimum conditions of N···C=O interaction, the nitrogen is on the bisecting plane of the C–C(O)–C angle and N···C=O angle is close to 109°.[12] The reason for the unfavorable arrangement in space of the Cl_1 and the 2-oxopropyl group is of course the geometrical requirements, bond angles and bond lengths. Thus we have to admit that, although the Cl_1 and the carbonyl carbon are located closely, the relative arrangement of the two groups is far from the optimum one. Therefore, the Cl···C=O interaction we observe in this compound may not be very strong. There is another possible reason why we do not observe the pyramidality of the 2-oxopropyl group. That is the steric reason. If it were to take a pyramidal structure, the repulsion between the atoms within the 2-oxopropyl group and the benzene ring B in the ±*sc* conformation would become formidable.

There is a piece of evidence, however, that there is an attractive interaction of a Cl···C=O type from the X-ray diffraction results. That is the bond lengths of the C=O. The C_{22}–O bond in the ±*sc* form is longer than that in the *ap* by 0.009 Å, although the difference is not listed in Table 5 because this is within 3σ. But it is tempting to consider that the C=O bond in the ±*sc* form is lengthened by the Cl···C=O interaction.

We conclude from both the population ratio in solution and the structural features observed by X-ray diffraction that there exists a Cl···C=O interaction in 1,2,3,4-tetrachloro-9-(2-oxopropyl)triptycene, if it is the ±*sc* form. The main driving force for the interaction is the charge transfer between the Cl_1 and the carbonyl carbon which are placed in proximity (3.035 Å), although their relative geometry is far from the optimum for the interaction. This interaction is strong enough to deform the 2-oxopropyl group in the ±*sc* conformation from that in the *ap* as discussed above. The C=O bond is lengthened by the Cl···C=O interaction in the ±*sc* form from that in the *ap*.

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